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IN THE UNITED STATES DISTRICT COURT
FOR THE EASTERN DISTRICT OF NEW YORK

FILED
IN CLERK'S OFFICE
U.S. DISTRICT COURT E.D. NY
LONG ISLAND OFFICE

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ALAN B. AMRON Pro Se

Plaintiff,

CIVIL ACTION NO. 12-11197

DEC 10 1997

-against-

CV- -

KEG

3M, MINNESOTA MINING AND
MANUFACTURING COMPANY

JURY TRIAL DEMANDED

Defendants.
-----X

CV 97 7281

COMPLAINT
JURISDICTION AND VENUE

PLATT, J.

ORENSTEIN, M.

1. This is an action brought for the purpose of determining an actual controversy under the patent laws of the United States, Title 35 U.S.C. sections 34, 42 and 102(a)(b)(g), and for unfair competition arising under the Trademark Act of 1946, 15 U.S.C. section 1051 et. al. as amended (hereinafter "the Lanham Act") and the Sherman Antitrust Act 15 U.S.C. section 1-7 and the Clayton Act 15 U.S.C section 1121. Venue in this district is proper under 28 U.S.C. Section 1391 and 1400 (b).

2. The jurisdiction for this case is diversity of citizenship, pursuant to T-28, U.S.C Section 1332.

PARTIES

3. Plaintiff, Alan B. Amron (hereinafter referred to as "Amron"), is an individual residing at 77 Horton Place, Syosset New York 11791.

4. Defendant, 3M MINNESOTA MINING AND MANUFACTURING COMPANY (hereinafter referred to as "3M"), is a corporation having a

principle place of business at 3M Center at 2501 Hudson Road Building #220-12W-01, St. Paul, Minnesota 55144-1000.

5. "Amron" has developed, designed, offered for sale, put into practice and or patented a wide variety of stationery, sporting good, novelty candy, children's toys, and games, for licensing such to industry. Among other inventions which Amron had conceived of, created, developed, designed, offered for sale and put into use before July 22, 1974 was "Press-on Memo" self stick removeable, repositionable and removable notes and its' specially developed adhesive which is made up of the following unique characteristics:

(a) Self Adhering (b) Repositionable (c) Low tack (d) Low or no adhesive build up (e) Never actually dries up, always stays tacky for multiple stick and re-stick use (f) Sticks on rough as well as smooth or flat surfaces such as wood, paper, glass, cardboard, fabric etc. (g) Self padding from sheet to sheet for stacking & padding (h) Self sticking (i) Removable and reapplicable to itself and other materials over & over again.

(see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

6. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on August 17, 1977 in a patent application serial number 825,259 and Patent Number 4,166,152 that this concept was first conceived of by William A. Baker et al. (see Exhibit #2) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (3) Three years after "Amron" had already conceived of, created, Developed and put into public

use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

7. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on August 13, 1987 in a patent application serial number 85,239 and Patent Number 4,855,170 that this concept was first conceived of by Wayne K. Darvell et al. (see Exhibit #4) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (13) thirteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

8. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on April 8, 1991 in a patent application serial number 681,655 and Patent Number 5,389,438 that this concept was first conceived of by John A. Miller et

al. (see Exhibit #5) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (17) seventeen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27))

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

9. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on April 27, 1992 in a patent application serial number 874,717 and Patent Number 5,378,536 that this concept was first conceived of by John A. Miller et al. (see Exhibit #6) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (18) eighteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27))

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

10. Defendant "3M", upon information and belief, has falsely

represented, by way of assignments, to the United States Patent and Trademark office on October 10, 1990 in a patent application serial number 595,319 and Patent Number 5,153,041 that this concept was first conceived of by George J. Clements et al. (see Exhibit #7) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (16) sixteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick, repositionable, removeable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

11. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on December 31, 1986 in a patent application serial number 948,095 and Patent Number 5,194,299 that this concept was first conceived of by Arthur L. Fry. (see Exhibit #8) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (12) twelve years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick, repositionable, removeable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

12. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on January 17, 1995 in a patent application serial number 373,585 and Patent Number 5,618,062 that this concept was first conceived of by Timothy A. Mertens et al. (see Exhibit #9) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (21) twenty one years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick, repositionable, removeable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

13. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on November 9, 1992 in a patent application serial number 973,039 and Patent Number 5,382,055 that this concept was first conceived of by Timothy A. Mertens et al. (see Exhibit #15) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657,

#659, #R-330 etc.

That was (18) eighteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick, repositionable, removeable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

14. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on July 1, 1994 in a patent application serial number 270,179 and Patent Number 5,571,617 that this concept was first conceived of by Terrence E. Coopridier et al. (see Exhibit #24) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (22) Twenty two years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

15. Defendant "3M", upon information and belief, has falsely

represented, by way of assignments, to the United States Patent and Trademark office on February 27, 1990 in a patent application serial number 485,630 and Patent Number 4,968,562 that this concept was first conceived of by Joaquin Delgado. (see Exhibit #25) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (16) Sixteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

16. Defendant "3M", upon information and belief, has falsely represented, by way of assignments, to the United States Patent and Trademark office on September 18, 1989 in a patent application serial number 407,092 and Patent Number 4,994,322 that this concept was first conceived of by Joaquin Delgado et al. (see Exhibit #26) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

That was (15) Fifteen years after "Amron" had already conceived of, created, Developed and put into public use on July 22, 1974 the reusable self stick removeable, repositionable notes know as "Press On Memo" and its' newly developed adhesive spray. (see Exhibits #1, #3, #12, #13, #14, #16, #17, #18, #19, #22 and #27)

The Defendant, by way of assignment, has represented that they were first to have conceived of this self stick, repositionable, removeable notes and its' special adhesive.

17. Defendant "3M", upon information and belief, has falsely claimed the date of first use date of September 25, 1974 on their trademark application serial number 300,787 for Post-it for notes and pads filed March 12, 1981 and issued on June 22, 1982 the registration number 1,198,694. (see Exhibit #20) In 3M Post-it Notes product numbers #653, #653A, #654, #654A, #655, #656, #657, #659, #R-330 etc.

For: "Stationery Notes containing adhesive on one side for attachment to surfaces."

"If, and when, an applicant falsifies an application submitted willfully to the Patent and Trademark office, and it is later shown to be false, the penalty is the immediate invalidation and withdrawal of that trademark registration from monopoly protection."

"3M", upon information and belief, has in fact willfully and maliciously falsified their application for a trademark "Post-it" for "Stationery notes containing adhesive on one side for attachment to surfaces." by claiming September 25, 1974 as the first use date, and the registration on Post-it for notes must now be invalidated and withdrawn.

BACKGROUND

18. In 1973 "Amron" invented, and patented, (U.S. Patent No. 4,022,350) the very first battery operated water gun toy,

which thereafter changed the pricing structure in the entire water gun toy and novelty industry. (see Exhibit #10 & #10a)

19. In 1973 "Amron invented, created, conceived of, developed, and in July 1974 offered for sale and put into public use a self stick, reusable, repositionable and removeable note pad called "Press On Memo" and its' specially developed adhesive "Stickem up" made up of the following unique characteristics:

(a) Self Adhering (b) Repositionable (c) Low tack (d) Low or no adhesive build up (e) Never actually dries up, always stays tacky for multiple stick and re-stick use (f) Sticks on rough as well as smooth or flat surfaces such as wood, paper, glass, cardboard, fabric etc. (g) Self padding from sheet to sheet for stacking & padding (h) Self sticking (i) Removable and reapplicable to itself and other materials over & over again.

A United States Patent was requested from a New York Patent attorney named Charles Marks, Esq. located on Fifth Avenue in New York City before July 1974.

20. It was requested of the Defendant 3M, by the Plaintiff, via certified return receipt letter dated October 29, 1997 (see Exhibit #11) to allow the Plaintiff the right to manufacture, license and sell his 1973 conceived, and 1974 offered for public sale, products and or to voluntarily withdraw or invalidate patents assigned to them for the related products known as "Post It Notes and its' adhesives".

"Conditions for patentability
novelty & loss of right to
Patent."

35 U.S.C. 102 (a) (b) (g).

21. Upon information and belief, the Defendant 3M has prevented other stationery industry manufacturers from making, producing and selling a self stick reusable, repositionable, removeable note pad via its' adhesives. The Defendant is preventing the Plaintiff "Amron" from making, using, licensing and selling his own creation, by not granting him the requested permission in his October 29, 1997 certified letter. (see Exhibit #11, #11a and #11b).

22. That as a result of the aforesaid conduct the Defendant "3M" was able to successfully restrain the trade, and the Plaintiff "Amron", by preventing them from making, selling, licensing or distributing memo pads and its' special adhesive with a removeable, repositionable, reusable self stick adhesive under Patents that should be invalidated under 35 U.S.C. 102 (a) (b) (g). The Defendant "3M" has, by not voluntarily invalidating their assigned patents, and by defending and enforcing them, gained an unfair business advantage over their competition. "3M" had an obligation to disclose, under the United States Patent and Trademark Office Rule 56 and under the Walker Process Case (87 S. Ct. 56-1966), the Plaintiffs earlier conception date, thereby invalidating their patents and allowing the Plaintiff, and the general public to manufacture, distribute and sell "like" memo pads with a removeable, repositionable, reusable self stick note sheets and the specially developed adhesive. As a

result of the aforesaid, the Press-on Memo self stick reusable, repositionable and removeable memo pad, and its' adhesive spray products, can not be made or sold by Amron and has caused the Plaintiff to suffer competitively in the stationery industry.

23. It is much more than just a coincidence that Amron did his mass mailing for Press-on Memos, which included actual samples and sales sheets to the entire stationery industry, which included 3M who was the maker of scotch tape, on or about July 22, 1974. 3M just happened to file for the Post-it Notes trademark in 1981, that was seven years after their claimed date of first use on the Post-it Note pads (see the attached Exhibit #20) of September 25, 1974 the very same date of first use claimed in their earlier Post-it trademark which had nothing to do with the new claim of use for Note Pads;

"paper and cardboard sheet material having adhesive coating on both sides thereof for attachment to walls or other vertical surfaces to hold displays or other messages in place"

24. Upon information and belief, 3M received Amrons' samples of Press-on Memos and its' adhesive spray two months prior to their September 25, 1974 date of claimed first use on the Post-it trademark for note pads.

25. It is obvious that 3M, upon information and belief, has illegally utilized Amron's Press-on Memo and its' adhesive spray samples, that they received via mailing and at

an International Inventors Expo held at the Americana hotel in New York, to manufacture what is known as Post-it Notes. This was done without the permission of Amron and specifically for 3M to gain an unfair business advantage over Amron by not having to pay him royalty.

26. 3M, upon information and belief, took Amrons' Press-on Memo and its' special adhesive concepts willfully and with malicious intent. It seems odd that 3M would wait seven (7) years from the claimed date of first use on September 25, 1974 of their trademark Post-it, until March 12, 1981 to actually file for the trademark on Post-it for Note pads. (see Exhibit #20).

27. That as a result of the aforesaid conduct the defendant 3M was able to successfully restrain the trade, by preventing Amron, and others, from manufacturing or selling these products. Upon information and belief, Amron was intentionally and maliciously kept out of the market, with his new products, in order for the Defendant "3M" to gain an unfair business advantage over their competition.

- a) On or about July 22, 1974 Amron mailed out samples of his "Press-on Memo" pads to the entire stationery industry, which included 3M.

3M received samples, at an International Inventors Expo where Amron personally demonstrated and gave samples of both the "Press-on Memo" sheets and the "Stickem up" spray adhesive used on the memos, for their evaluation and possible license.

- b) On March 12, 1981, seven years later, 3M filed for a trademark on Post-it for Note Pads, claiming September 25, 1974 as their date of first use for the Post-it trademark registration.

Relying on 3M's boldly claimed September 25, 1974 date of first use for the trademark of Post-it for Note Pads, that is two months after Amron had sent 3M a sample of his Press-on Memo pads and gave a sample to 3M's representative of both the memo pads and its' spray adhesive for their evaluation. Press-on Memo and Post-it Notes both have the exact same characteristics (see the attached chart in Exhibit #22).

28. Upon information and belief 3M, the Defendant, has been illegally benefiting from Amrons' invention/conception for years.

THEREFORE, based on the above information and beliefs of Fraud and Deceit on the part of the Defendant 3M, it is clear that 3M has, for the past several years, illegally and under false pretenses, claimed conception of self stick removable, repositionable, reusable pressure sensitive note pads and sheets and its' related adhesive. Which is The Novelty and Utility of all of these patents.

"To gain an unfair business advantage over all their competition."

COUNT I -- DECLARATORY JUDGEMENT

29. Plaintiff incorporates the averment of paragraphs 1

through 28 as if fully restated herein.

30. Defendant, "3M", upon information and belief, has falsely filed, through assignments for patent numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and trademark registration number 1,198,694 falsely claiming better dates of first conception than that of the Plaintiff "Amron".

31. The Defendants assigned United States Patent Numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and trademark registration number 1,198,694 should all be declared invalid, under 35 U.S.C. 102 (a) (b) & (g). due to the Plaintiff's earlier conception and put into use dates, and upon information and belief, 3M had made false claims of first use dates on their applications for these patents and trademark.

COUNT II -- DECLARATION OF INVALIDITY
OF PATENT NUMBERS 4,166,152, 4,855,170, 5,382,055,
5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438
5,571,617, 4,968,562 4,994,322 AND
TRADEMARK REGISTRATION NUMBER 1,198,694

32. Plaintiff incorporates the averment of paragraphs 1 through 31 as if fully restated herein.

33. The Defendant, by way of assignments, upon information and belief, has represented that they should be protected under United States Patents and Trademarks, and that they

have invented and or discovered the technology in patent numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and first use date of Trademark Post-it for Notes Registration Number 1,198,694 and have the right to licence, manufacture, distribute, sell and profit from and protect them under that monopoly protection.

34. The Defendant, by way of assignment and upon information and belief, has conspired to file false patent applications claiming conception, thereby causing Amron and others in the stationery industry great financial injury, strictly to gain an unfair business advantage over their competition and to hold claim on the illegally held monopoly of this technology.

COUNT III -- UNCLEAN HANDS/UNFAIR COMPETITION

35. Plaintiff incorporates the averment of paragraphs 1 through 34 as if fully restated herein.

36. Upon information and belief, The Defendants actions were for the purpose of gaining an unfair business advantage over their competition.

37. The Plaintiff "Amron" has suffered irrevocable financial injury due to the, upon information and belief, false patent filings of the Defendant, and the false and misleading use of their assigned Patents rights, and are acts of unfair competition under the common law of the State of New York.

COUNT IV -- VIOLATION OF U.S.C TITLE 35
SECTION 34, 42 and 102 (a)(b)&(g).

38. Plaintiff incorporates the averment of paragraphs 1 through 37 as if fully restated herein.

39. The actions of the Defendant, have caused great financial damage, embarrassment and frustration to Amron.

40. An invention may be anticipated by disclosure of an earlier conception, put into use and offered for sale date at least one (1) year prior to its filing date of an application for a United States Patent. (Title 35 U.S.C. Section #34)

COUNT V -- PUNITIVE DAMAGES

41. Plaintiff incorporates the averment of paragraphs 1 through 40 as if fully restated herein.

42. Upon information and belief, the intentionally damaging and conspired actions of the Defendant "3M", by their assignments of these patents, was deliberate and malicious with a bad motive for reckless indifference to their competition and to the Plaintiff "Amron" and was done without any justification.

COUNT VI -- ANTITRUST ACTION
UNDER SECTION 2 SHERMAN ACT

43. Plaintiff incorporates the averment of paragraphs 1 through 42 as if fully restated herein.

44. United States Patent numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and Trademark Registration Number 1,198,694 were, upon information and belief, issued based on applications filed Fraudulently and must be declared invalid.

45. 3M's 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 Patents and Trademark registration number 1,198,694 were, on information and belief, the basis for Defendants' attempt to monopolize, and their monopolization, of the field of Memo/Note pads sheets and its' related adhesive. They obtained such monopoly power by advising of their ownership of intellectual patent rights, thereby threatening others with the filing of infringement litigations.

46. Upon information and belief, a prior art, "Amrons' Press-on Memo pad" and its' related adhesive product, was known to the Defendants before and during the pendency of the 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 Patents and Trademark registration number 1,198,694 and their applications, specifically in July of 1974 when Amron did a 2,000 piece mass mailing to everyone connected to the stationery industry. The Defendant, "3M", was known as the maker of Scotch Tape, so it was included as one of the

2,000 piece mailing sent out to the entire stationery industry.

47. The Defendants', under Patent and Trademark Office Rule 56 and under the Walker Process Case (87 S.Ct. 56-1966), had a duty to disclose material prior art to the Patent Office and, upon information and belief, they did not do so.

48. The Defendants' maintenance and enforcement of their Patents 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and their Trademark Registration Number 1,198,694 which were, upon information and belief, obtained by fraud on the Patent Office, is the basis for this action under section 2 of the Sherman Act. Plaintiff is an injured party and therefore makes this treble damage claim under section 4 of the Clayton Act. The other elements of a section 2 Sherman Act violation are present, as Defendants exercised the exclusionary power of illegal Patents 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and Trademark Registration Number 1,198,694 over the relevant market for the products involved, namely Post-it Notes self stick reusable, removable, repositionable sheets and its' related adhesive. That is a separate and commercially important market.

49. That Defendant had a duty to disclose, under Patent and Trademark Office Rule #56, but upon information and belief,

failed to so disclose, and upon information and belief the Defendants have prevented Amron and the trade from making this product and thereby restrained trade.

50. The Defendants' maintenance and enforcement of the Patent numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and Trademark Registration Number 1,198,694, upon information and belief, was acquired by Fraud on the Patent Office, and is a violation of the aforesaid Sherman Act (sections 1-7) and Clayton Act (section 1121).

PRAYERS FOR RELIEF

WHEREFORE, Plaintiff demands judgement against the Defendant, "3M":

A. That the Defendant, 3M, publicly apologize to Alan Amron for causing him major financial injury, pain, suffering and embarrassment.

B. That the Defendant 3M's assigned Patent numbers 4,166,152, 4,855,170, 5,382,055, 5,378,536, 5,153,041, 5,194,299, 5,618,062, 5,389,438, 5,571,617, 4,968,562, 4,994,322 and Trademark Registration Number 1,198,694 be declared invalid and all royalties and or financial benefits received from the sales of those patent rights, and teachings, be immediately paid directly to "Amron".

C. That judgement be entered for compensatory damages

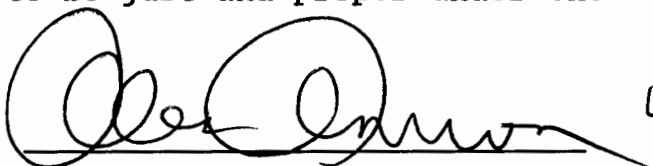
in favor of the Plaintiff and against the Defendant, for no less than **NINE MILLION DOLLARS**.

D. That a judgement be entered for punitive damages in favor of the Plaintiff and against the Defendant, for no less than **THREE MILLION DOLLARS**.

E. That judgement be entered in favor of the Plaintiff and against the Defendant, for treble damages in a sum of no less than **THIRTY SIX MILLION DOLLARS**.

F. That judgement be entered in favor of the Plaintiff and against the Defendant, for out of pocket expenses and costs relating to this case in the sum of **FIFTY THOUSAND DOLLARS**.

G. That the court order such other and further relief as may be deemed by the Court to be just and proper under the circumstances.



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Defendant,

3M, Minnesota Mining & Manufacturing Company
c/o Mr. Gary L. Griswold, Esq.
Office of Intellectual Property Chief Counsel
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EXHIBIT LIST TO SUPPORT THE ATTACHED COMPLAINT

EXHIBITS #1, #1a, #1b, #1c, #1d and #1e.

#1 November 29, 1973 Amron originally contacted a chemist to develop his new adhesive for his Press-on Memo sheets.

#1a Proof of date on actual envelope post marked of that letter.

Color Comparison charts of;

#1b Samples of actual "Press On Memo sheets" from an original pad, along side a 3M "Post It Note sheet"

#1c Another example comparison Press-on and Post-it

#1d Post-it notes examples front and back TM v. R

#1e Post-it notes advertisement introduction to the industry

EXHIBIT #2

United States Patent #4,166,152 validity in question.

EXHIBITS #3, #3a, #3b and #3c.

Amrons' conception, development, offer for sale and put into use date sample items. "PRESS ON MEMO".

#3 Postmarks to prove dates.

#3a Actual Envelope used in mailings.

#3b Actual Sales Flyers mailed and handed out.

#3c Press-on Memo sheet sample mailed and handed out.

EXHIBIT #4

United States Patent #4,855,170 validity in question.

EXHIBIT #5

United States Patent #5,389,438 validity in question.

EXHIBIT #6

United States Patent #5,378,536 validity in question.

EXHIBIT #7

United States Patent #5,153,041 validity in question.

EXHIBIT #8

United States Patent #5,194,299 validity in question.

EXHIBIT #9

United States Patent #5,618,062 validity in question.

EXHIBIT #10 and #10a. For background;

#10 AMRON United States Patent #4,022,350 for the battery operated water gun invention.

#10a AMRON'S other invented created and licensed products.

EXHIBIT #11

#11 Letter dated October 29, 1997 from Amron sent certified return receipt requesting permission from 3M to allow Amron to manufacture, license or sell his conception and creation and or for 3M to notify the United States Patent and Trademark Office of an earlier conception and put into use date, thereby invalidating their patents.

#11a Proof of Certified mailing.

#11b Returned receipt from 3M.

EXHIBIT #12

In 1974 Amron had an investor by the name of Jeffrey Brown who was a partner in the development and sale of this new product. See his Affidavit attached in support of the attached complaint.

EXHIBIT #13

In 1974 Amron had his general counsel at the time Mr. Michael Solomon, Esq., who is now a Judge in New York, set up a Corporation (New York State Corporation name "PRESS ON MEMO LTD.) with its' only and specific purpose to develop, manufacture and offer for sale Amrons' invention called "Press On Memos" to the stationery industry and world. See his Affidavit and certificate of Corporation from New York State in support of the attached complaint.

EXHIBIT #14

On July 22, 1974 Amron personally opened a post office box number 302 in Rockville Centre Long Island New York under the name of his product and Corporation "Press On Memo Ltd." for the specific purpose of receiving orders and correspondences from the mass mailings and advertisements that were directed to the entire stationery industry.

EXHIBIT #15

United States Patent #5,382,055 validity in question.

EXHIBIT #16

Amron showed his new invention at the New York Americana hotels International Inventors Expo and introduced his new invention to the world and its general industries that had attended. A representative of 3M was shown "Press-on Memos" at that show, and was given samples of both the Press-on Memo sheets and its' newly developed adhesive spray the memos used to work so well, to take back with him to show to his boss. They never did get back to me.

EXHIBIT #17

Amron met with in person, and spoke to on the telephone, two major mail order companies and a mail order convention consultant about selling my "Press On Memo Pads".

- (a) J. Carlton Mail order company in New York.
- (b) Jay Norris mail order company in Freeport Long Island, Joel Jacobs owner.
- (c) National Mail Order Merchandise Show, Bernard Lane.
(see this letter attached here)

EXHIBIT #18, #18a, and #18b.

Amron did a 2,000 piece mailing through the Mass Mailing company in New York City, Mr. Dick Freudenhien and Sol Rebach, to all stationery retail and manufacturing buyers, introducing and offering for sale the new "Press On Memo pads" with sales brochure and a sample "Press On Memo" self stick removeable, repositionable, reusable note sheet enclosed in each mailing.

#18 Actual Envelope

#18a Sales Sheet

#18b Sample of self stick repositionable, reusable and removable memo sheet.

EXHIBIT #19

This is the Original artwork of Amrons' concept. On or about February 1974 Steve Grossman, a graphic artist who did all the artwork designs for the Benihana restaurants, did this attached original concept rendering for Amrons. Steve Grossman and Dave Warren did the actual printing of the Mass mailing envelopes, sales sheets and sample "Press On Memo sheets", as seen in EXHIBITS #3a, #3b and #3c.

EXHIBIT #20

Trademark for Post-it Note Pads was filed on March 12, 1981 Serial number 300,787 and Registration number 1,198,694 Registered June 22, 1982. Claimed date of first use of the Post-it mark on pads was September 25, 1974.

EXHIBIT #21

Trademark for Post-it two sided paper and cardboard product was filed on December 29, 1975 Serial number 72,879 and Registration number 1,046,353 registered August 17, 1976 for the Post-it mark "...having adhesive coating on both sides thereof..." on paper and cardboard products with the very same claimed September 25, 1974 date of first use as in the six years later application for Post-it Notes date of first use.

EXHIBIT #22

Product Comparison of Characteristics Chart Press-on Memo v. Post-it Notes. Both are exactly the same, in novelty and utility and inventiveness they:

"both do the same thing"
"the same way"
"to get the same result."

"An invention which does not combine three essential elements of novelty, utility and nonobviousness should not be given privileged monopolistic status of a patent".

EXHIBIT #23

Amron, the Pro Se Plaintiffs, Affidavit in support of this complaint.

EXHIBIT #24

United States Patent #5,571,617 validity in question.

EXHIBIT #25

United States Patent #4,968,562 validity in question.

EXHIBIT #26

United States Patent #4,994,322 validity in question.

EXHIBIT #27, #27a, #27b, #27c and #27d.

"Stickem up" spray repositionable, reusable and removable self stick low tack adhesive used on the Amron Press-on Memo sheets developed in 1973 to his specifications.

EXHIBIT #28 and #28a.

#28 Actual original purchase order from a photo manufacturer and supplier ordering 150 dozen cans of Amron's special adhesive spray.

#28a Actual packing slip invoice shipped with the order.

EXHIBIT #29 a-s

A two month sampling, from March 14, 1975 through May 19, 1975 of packing slip invoices for 20 companies that bought the Amron developed new adhesive with its' following unique characteristics:

- (a) Self Adhering
- (b) Repositionable
- (c) Low tack
- (d) Low or no adhesive build up
- (e) Never actually dries up, always stays tacky for multiple stick and re-stick use
- (f) Sticks on rough as well as smooth or flat surfaces such as wood, paper, glass, cardboard, fabric etc.
- (g) Self padding from sheet to sheet for stacking & padding
- (h) Self sticking
- (i) Removable and reapplicable to itself and other materials over & over again."



DR. DAVID W. YOUNG, HON. AIC

CHEMICAL CONSULTING SERVICE
RESEARCH AND DEVELOPMENT

1409 JOHN HANCOCK CENTER
875 NORTH MICHIGAN AVENUE
CHICAGO, ILLINOIS 60611
(312) 649-1310

November 29, 1973

Mr. Alan B. Amron
Refrigeration Alarm Systems Corporation
31 South Grove Street
Freeport, New York 11520

Dear Mr. Amron:

With reference to your memo of November 14, the cost of a program for developing a composition suitable for your invention would be \$750.00, for research and product formulations; plus any cost for materials used. If you plan to proceed with a patent, there would be an additional cost of \$1,000 - \$1,500 for filing with the Government Patent Office.

*1/3 Down
30 Day*

I greatly appreciate your considering my office for assistance in developing a cement system for Con-Tactless. I would like to arrange a meeting to discuss this program. Also, before such meeting a sample of Tactless and Con-Tactless, as shown in Figures 1 and 2 of your report. Any additional information and descriptions would be most helpful.

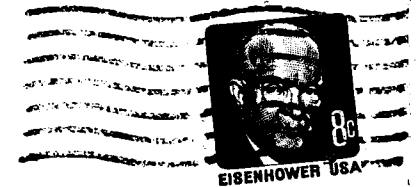
Sincerely,

DAVID W. YOUNG

:lp

DR. DAVID W. YOUNG, HON. AIC

1409 JOHN HANCOCK CENTER
875 NORTH MICHIGAN AVENUE
CHICAGO, ILLINOIS 60611



Mr. Alan B. Amron
Refrigeration Alarm Systems Corporation
31 South Grove Street
Freeport, New York 11520

Self stick repositionable strip

Tiny little adhesive islands
of pressure sensitive material

Back

Self stick repositionable strip

Tiny little adhesive islands
of pressure sensitive material

Back

Front

Post-it Notes
introduced by 3M
in 1981

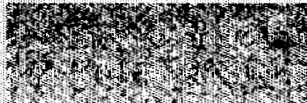


Front

Press-On Memo
introduced by Amron
in 1974



Post-it Notes



**3x Magnified
adhesive**

Press-On Memos



**3x Magnified
adhesive**

**Product Adhesive
Comparison Chart**

Self stick removable glue strip

Tiny little adhesive islands
of pressure sensitive glue...

Back

Self stick removable glue strip

Tiny little adhesive islands
of pressure sensitive glue...

Back

Front

Post-it Notes
introduced by 3M
in 1987

Post-it
Note Pad

Self-Stick Removable Notes

654 1 Pad (100 sheets)
3 in x 3 in (76.2mm x 76.2mm)

3M

To Open ▼

Front

Press-On Memo
introduced by Amron
in 1974



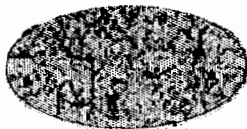
THE
MAGIC • TOUCH

YOUR INVITATION
TO INSTANT PROFIT!
IT'S PRACTICAL, IT'S ATTRACTIVE,
IT'S EASY TO HANDLE...

JUST JOT DOWN YOUR MEMO, TEAR OFF, PLACE ANYWHERE.
TOUCH THE MAGIC 'M' AND PRESTO IT STAYS. IT'S THAT EASY.
THIS NOW ALLOWS YOU TO HANG YOUR MEMO WITHOUT THE
USE OF TAPES, PINS OR MAGNETS.

WITH OUR EXCITING ADVERTISING
CAMPAIGN REACHING A MARKET
THAT'S ENDLESS...IT ADDS UP TO BIG
PROFITS! THAT'S NOT MAGIC...
THAT'S GOOD BUSINESS.

Post-it



3x Magnified

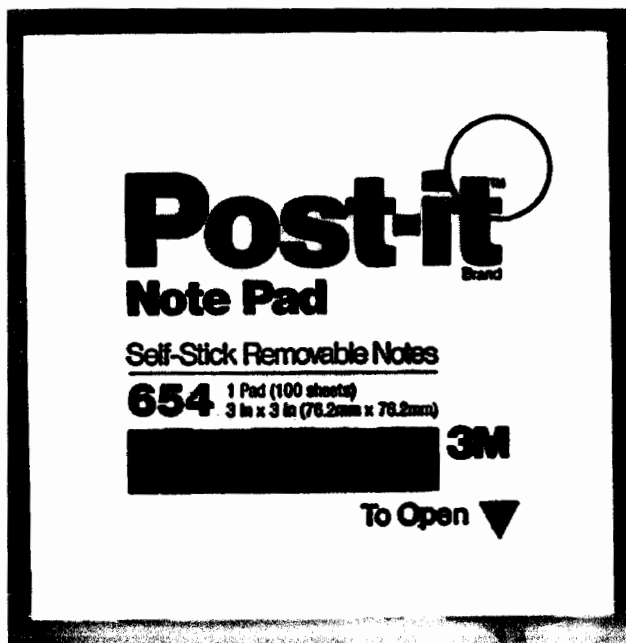
Press-On



3x Magnified

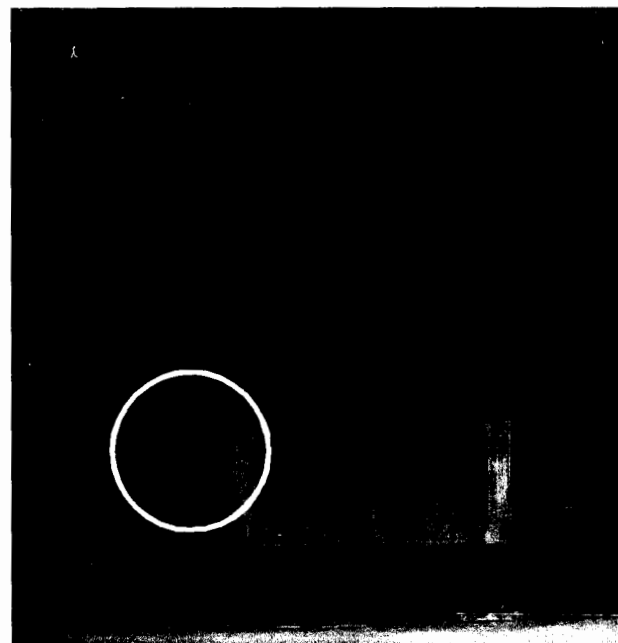
**Product
Comparison
Chart**

Post-it Note Pad first introduced in 1987

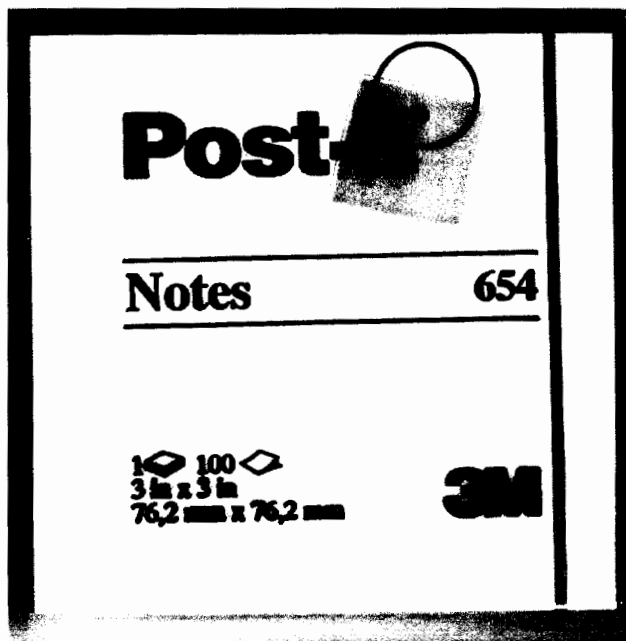


Front

1987
TM

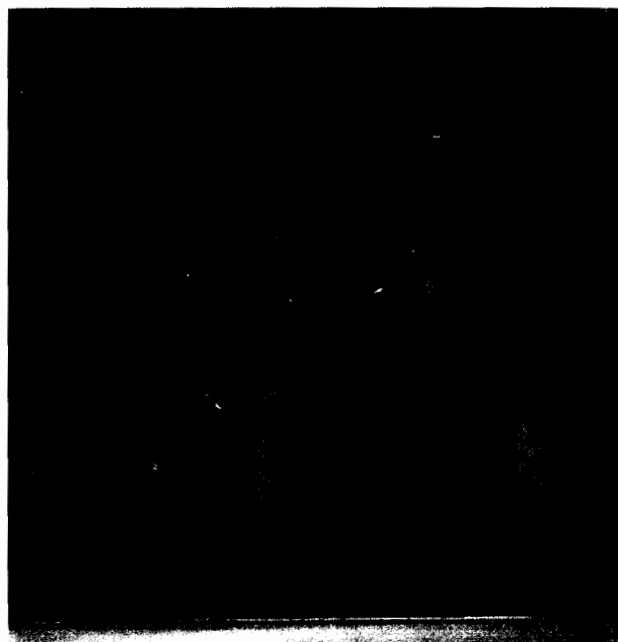


Back



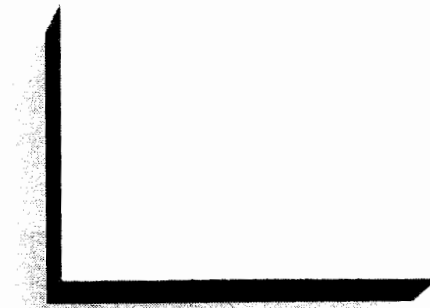
Front

1997
®



Back

A giant communications breakthrough. (Actual size)



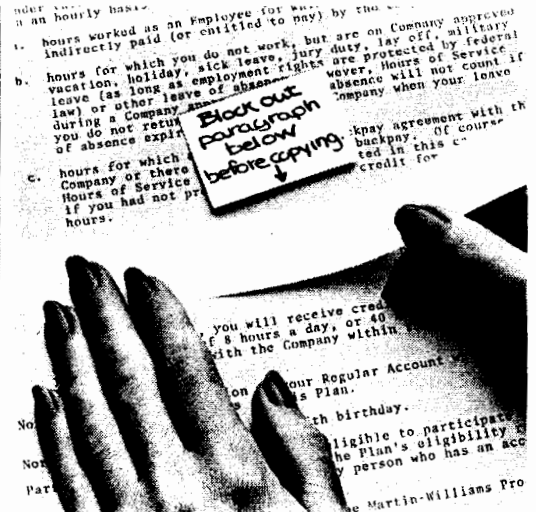
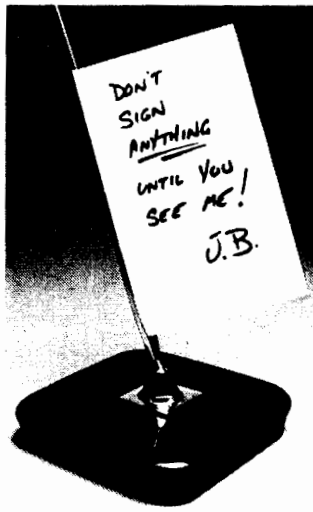
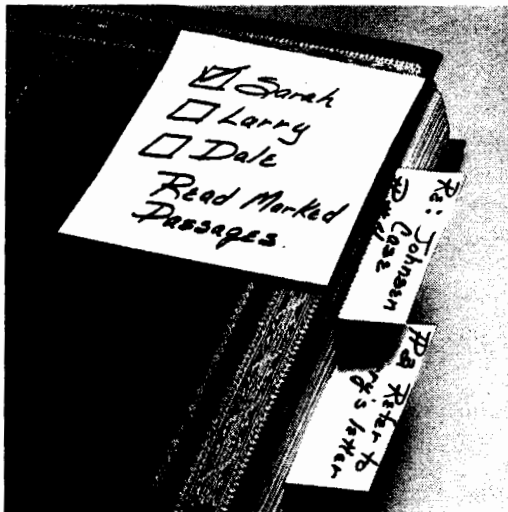
Introducing new Post-it® Notes from 3M. They look like ordinary note paper. But they're far more convenient. They have an exciting kind of adhesive on the back which allows them to be attached without staples, paper clips or tape.

They'll stick to almost any surface. Then come unstuck when you want them to. So you can use them to attach notes to correspondence, flag pages in books and magazines, or as routing slips.

Post-it Notes are available in three sizes: 3" x 5", 3" x 3", and 1½" x 2". There's even Post-it Note Tape for blind-copying letters or memos.

Free sample.

Ask the person who buys your supplies to get a free sample from your office supply dealer. Or look in the Yellow Pages under "Office Supplies" for a dealer near you.



"Scotch" and "Post-it" are registered trademarks of 3M.

New Post-it® Notes

3M

United States Patent [19]

[11] 4,166,152

Baker et al.

[45] Aug. 28, 1979

[54] TACKY POLYMERIC MICROSPHERES

[56]

References Cited

[75] Inventors: William A. Baker, Stillwater; Warren D. Ketola, St. Paul, both of Minn.

U.S. PATENT DOCUMENTS

3,513,120 5/1970 Pohlemann et al. 526/200
4,049,604 9/1977 Morehouse et al. 526/203

[73] Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.

Primary Examiner—Harry Wong, Jr.
Attorney, Agent, or Firm—Cruzan Alexander; Donald M. Sell; Gerald F. Chernivec

[21] Appl. No.: 825,259

[57]

ABSTRACT

[22] Filed: Aug. 17, 1977

[51] Int. Cl.² C08F 20/10; C08F 20/14

[52] U.S. Cl. 428/522; 260/29.6 R;
526/200; 526/201; 526/203; 526/328;
526/328.5

[58] Field of Search 526/328.5, 200, 201,
526/203, 328; 260/29.6 R; 428/522

Infusible, solvent-insoluble, solvent-dispersible, inherently tacky, elastomeric polymeric microspheres which are formed from non-ionic monomers and comprise at least one oleophilic water-emulsifiable alkyl acrylate or methacrylate ester, and a suspension polymerization technique for producing the microspheres, which includes the use of an ionic suspension stabilizer.

10 Claims, No Drawings

TACKY POLYMERIC MICROSPHERES

BACKGROUND OF THE INVENTION

This invention relates to inherently tacky, elastomeric, solvent-dispersible, solvent-insoluble, polymeric microspheres and a process for preparing same.

In U.S. Pat. No. 3,691,140 to Silver, there are disclosed inherently tacky acrylate copolymer microspheres comprising a major portion of at least one alkyl acrylate ester and a minor portion of an ionic monomer.

As discussed in the Silver patent, the microspheres can be unexpectedly prepared by suspension polymerization techniques, which historically have been considered unsuitable for preparation of tacky polymers. In the technique described by Silver, the microspheres are prepared utilizing an emulsifier in an amount greater than the critical micelle concentration in the absence of externally added protective colloids or the like. The Silver microspheres are copolymeric in nature and require an ionic comonomer as an essential component thereof.

It has now been found that inherently tacky microspheres having physical properties similar to those of the Silver patent, i.e., inherent tack, infusibility, solvent dispersibility, and solvent insolubility, can be prepared which are not limited to copolymers, but may also be homopolymers, and do not contain an ionic comonomer. The microspheres are prepared by aqueous suspension polymerization, but have as an essential ingredient in their preparation a hereinafter defined suspension stabilizer.

SUMMARY OF THE INVENTION

In accordance with the invention there are provided inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric polymeric microspheres which are formed from non-ionic monomers and are comprised of at least one oleophilic, water-emulsifiable alkyl acrylate or methacrylate ester.

The microspheres of the invention are prepared by an aqueous suspension polymerization technique utilizing emulsifiers in an amount greater than the critical micelle concentration, in combination with an ionic suspension stabilizer.

DETAILED DESCRIPTION OF THE INVENTION

Useful alkyl acrylate or methacrylate ester monomers are those which are oleophilic, water-emulsifiable, of restricted water-solubility, and which, as homopolymers, generally have glass transition temperatures below about -20°C . Exemplary alkyl acrylate and methacrylate ester monomers which are suitable for preparation of the microspheres of the invention include n-butyl acrylate, secbutyl acrylate, 2-methyl butyl acrylate, 4-methyl-2-pentyl acrylate, 2-ethyl hexyl acrylate, isooctyl acrylate, isodecyl methacrylate, and the like. Alkyl acrylate and methacrylate ester monomers with glass transition temperatures higher than -20°C . (i.e., butylmethacrylate, isobornyl acrylate, or the like) may be utilized in conjunction with one of the above-described monomers as long as the glass transition temperature of the resultant polymer is below about -20°C .

Additionally, the tacky nature of the microspheres can be varied by inclusion of a minor portion of a non-acrylate or methacrylate ester comonomer which is

non-ionic and water insoluble, such as divinyl benzene, N-t-octylacrylamide, etc.

The microspheres of the invention are prepared by an aqueous suspension polymerization technique utilizing at least one emulsifier in a concentration greater than the critical micelle concentration. The critical micelle concentration is that minimum emulsifier concentration necessary for the formation of micelles, and is slightly different for each emulsifier, usable concentrations typically ranging from about 1.0×10^{-4} to about 3.0 moles per liter.

The emulsifiers used for the successful preparation of the inherently tacky microspheres of this invention are preferably anionic in nature, typical examples being sodium dodecylbenzene sulfonate, sodium salts of alkylaryl ether sulfonates, and the like. Non-ionic emulsifiers, e.g., ethoxylated oleyl alcohol, can also be utilized alone or in conjunction with anionic types. In this latter instance, it is preferred that the anionic emulsifier predominates.

Catalysts or polymerization initiators for polymerizing the monomers to provide the microspheres of the invention are those which are normally suitable for free-radical polymerization of acrylate monomers, and which are oil-soluble and of very low solubility in water such as, for example, benzoyl peroxide. The use of water-soluble catalyst may cause formation of substantial amounts of latex, the extremely small particle size and solvent solubility of which are undesirable.

Concentration of catalysts may affect sphere quality and therefore, should be on the order of about 0.15 to about 0.66 percent by weight of the total monomers, and more preferably about 0.25 to about 0.45 percent by weight. Catalyst concentrations below about 0.15 percent by weight may tend to cause agglomeration of the microspheres, whereas concentrations greater than about 0.66 percent may result in low molecular weight polymers which do not exhibit all of the desired properties.

Ionic suspension stabilizers that assist in the preparation of the microspheres can be characterized by an interfacial tension of at least about 15.0 dynes per centimeter. Interfacial tension herein means the value determined between the monomer phase and a 1.0 percent by weight aqueous solution of the stabilizer. To determine the interfacial tension, a standard test, ASTM #D-1331-56, entitled "Standard Methods of Tests for Surface and Interfacial Tension of Solutions of Surface Active Agents" can be utilized. If the interfacial tension between the monomer phase and the 1.0 percent by weight aqueous solution of stabilizer falls below about 15.0 dynes per centimeter, there is insufficient stabilization of the final polymerized droplets and agglomeration may occur.

The approximate concentration of any single stabilizer required for successful preparation of the tacky microspheres of this invention can also be determined by the value of the interfacial tension. Typically, increasing interfacial tension values between the monomer phase and the aqueous stabilizer phase corresponds to a reduction in required concentration of the particular stabilizer for the successful preparation of the microspheres. Stabilizer concentrations greater than about 10 percent by weight based on the monomer may tend to provide less than optimum properties to the resultant suspension.

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Exemplary stabilizers include salts of polyacrylic acid of greater than about 5000 molecular weight (e.g., the ammonium, sodium, lithium, and potassium salts), carboxy modified polyacrylamides (e.g., "Cyanamer A-370" from American Cyanamid), copolymers of acrylic acid and dimethylaminoethylmethacrylate and the like, quaternary amines (e.g., General Aniline and Film's "Gafquat 755", a quaternized polyvinyl-pyrrolidone copolymer, or Union Carbide's "JR-400", a quaternized amine substituted cellulosic), and carboxy modified cellulosics (e.g., Hercules' "Natrosol CMC Type 7L", sodium carboxy methylcellulose). The following is a table indicating representative stabilizers, their interfacial tension with the monomer phase, and the concentration level found to be required for successful microsphere preparation.

Table I

| Stabilizer Trade Name | Class | Interfacial Tension Between Isooctyl-acrylate and 1.0% Solution of Stabilizer in H ₂ O dynes per cm. | Approximate Level for Successful Preparation of Isooctyl-acrylate Homopolymer (Weight Percent Based on Monomer) |
|-----------------------|---|---|---|
| None | 50/50 copolymer of acrylic acid and dimethylamino ethyl-methacrylate | 21.2 | 1.0% |
| Good Rite K714 | Polyacrylic acid (neutralized with ammonia) | 21.0 | 1.0% |
| GAF Gafquat 755 | Quaternized polyvinyl pyrrolidone copolymer | 18.2 | 1.0% |
| Union Carbide JR-400 | Quaternized cellulosic | 18.5 | 1.0% |
| Cyanamer A-370 | Carboxy modified polyacrylamide | 21.0 | 3.0% |
| Natrosol CMC Type 7L | Sodium carboxy-methylcellulose | 19.8 | 5.0% |
| Gantrez HYM | Copolymer of polyvinylmethylether and maleic anhydride (neutralized with ammonia) | 15.4 | 10.0% |

Although some stabilizers may function at levels greater than 10 percent based on monomer, the resultant suspensions may become undesirable for several reasons, e.g., they may contain too large an amount of undesirable latex polymer. Furthermore, control of final particle size can become difficult because of the high viscosities involved and excess concentration levels may also lead to detackification of the resultant polymer spheres.

Following polymerization, the aqueous suspension of polymer microspheres is stable to agglomeration or coagulation under room temperature conditions. The polymer suspension may have non-volatile solids contents from about 10 to about 50 percent by weight. Upon prolonged standing, the suspensions may separate into two phases, one phase being aqueous and substantially free of polymer, the other phase being an aqueous suspension of the polymer spheres. The degree and type of separation is dependent on the density of the resultant polymers. Separation of the polymer phase provides a

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low viscosity aqueous suspension having a non-volatile solids content on the order of about 75 percent which, if shaken with water, will readily redisperse.

If desired, the aqueous suspension of microspheres may be utilized immediately following polymerization to provide inherently tacky coatings or adhesives. The aqueous suspension may also be coagulated with methanol, saturated salt solutions, or the like, followed by washing and drying. These dried polymer spheres, with sufficient agitation, will readily disperse in a wide variety of common organic solvents. Once the polymer is dried, however, it is not redispersible in water.

The polymer microspheres are typically small in size, having diameters in the range of about 1 to about 250 microns, the diameter of the majority of the spheres being in the range of from about 5 to about 150 microns. The spheres are normally tacky and elastomeric, are insoluble in organic solvents, and form dispersions in most common solvents except such highly polar solvents as water, methanol, and ethanol. Typical useful solvents are ethyl acetate, tetrahydrofuran, heptane, 2-butanone and other ketones, benzene, cyclohexane, and isopropanol and higher alcohols. When dispersed in such solvents, the microspheres absorb the solvent and swell to about twice their original diameter, or about 8 times their original volume. After dispersion, the microspheres, which contain about 80 percent solvent, remain homogeneously dispersed for extended periods of time. A force applied directly to one of the polymer spheres will deform it; however, the spherical shape is resumed upon release of the stress. Upon being heated, the spheres typically do not melt or flow, but retain their integrity until their carbonization temperature is reached.

The microspheres can be utilized in aerosol adhesives, they can be applied to substrates as an adhesive, they can be mixed with binder materials, and placed on substrates to provide repeatedly reusable adhesive surfaces, such as disclosed in U.S. Pat. No. 3,857,731, and they can be combined with a hot melt adhesive on a substrate to provide a positionable hot melt adhesive system, as is disclosed in commonly assigned and co-pending U.S. application Ser. No. 742,743 of Loder et al.

The invention will now be more specifically described by the following non-limiting examples, wherein all parts are by weight unless otherwise specified.

EXAMPLE I

To a 3 liter, 3-necked flask equipped with thermometer, reflux condenser, mechanical stirrer, and vacuum and nitrogen inlet tube, were charged 1407.7 grams of deionized water and 27.0 grams of "Good Rite K714" (tradename for a 15 percent solids aqueous solution of polyacrylic acid of 200,000 molecular weight, commercially available from the B. F. Goodrich Co.). The contents of the flask were then agitated until all of the polyacrylic acid was dissolved, and concentrated ammonium hydroxide was added thereto until a pH of 7.0 was obtained.

To this solution were added 500 grams of isooctylacrylate and 1.75 grams of "Lucidol 70" (tradename for a 70 percent active benzoylperoxide catalyst commercially available from Lucidol Division, Pennwalt Corporation). A vacuum was then placed on the contents of the flask, the pressure therein being drawn to 28 inches

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5

of mercury and held for one minute to assure removal of dissolved air and oxygen. The vacuum was then broken with nitrogen. A nitrogen purge was kept over the batch throughout the reaction period. Five grams of an emulsifier, "Siponate DS-10" (tradename for a commercially available sodium dodecyl benzene sulfonate, commercially available from Alcolac, Inc.) were added to the mixture and the agitation was set at 400 rpm.

The batch was then heated to 60° C. and maintained for 16 hours. As the temperature initially approached 60° C., a mild exotherm was noted to approximately 70° C., at which time cooling was not applied until cessation of the exotherm, after which the flask was maintained at 60° C. After the 16 hour period, the suspension was allowed to cool to room temperature, and the resulting suspension polymer was filtered through a 60 mesh screen. The resultant homopolymer contained 25.14 percent solids, and upon standing, the polymer spheres creamed to the surface but were easily redispersed. Average particle size of the polymer spheres was from 10 to 20 microns.

EXAMPLES 2-5

These examples were prepared utilizing the equipment, monomer, and general procedure outlined in Example 1 and illustrate the use of various stabilizers and anionic emulsifiers. The microspheres were found to be inherently tacky, infusible, and insoluble but dispersible in organic solvents.

Table II

| Example | Emulsifier | Stabilizer | Percent Solids | Average Polymer Particle Size, Microns |
|---------|--|---|----------------|--|
| 2 | 5g sodium dodecylbenzene sulfonate | 5g 50-50 molar ratio copolymer of acrylic acid and dimethylaminoethylmethacrylate | 24.3 | 66.1 |
| 3 | 5g sodium dodecylbenzene sulfonate | 5g GAF Gafquat 755 | 25.8 | 52 |
| 4 | 5g sodium dodecylbenzene sulfonate | 15g Cyanamer A-370 from American Cyanamid | 25.2 | 8.7 |
| 5 | 5g sodium salt of alkyl aryl polyether sulfonate | 5g 50-50 molar ratio copolymer of acrylic acid and dimethylaminoethylmethacrylate | 27.2 | 63.8 |

EXAMPLE 6-9

These examples were prepared utilizing the equipment and procedures outlined in Example 1, and illustrate the preparation of inherently tacky microspheres from different monomers, using 5 grams of sodium dodecylbenzenesulfonate as the emulsifier, and 5 grams of a 50/50 mole ratio copolymer of acrylic acid and dimethylaminoethylmethacrylate as the stabilizer.

Table III

| Example | Monomer | Percent Solids | Average Polymer Particle Size, Microns |
|---------|----------------------|----------------|--|
| 6 | n-butylacrylate | 19.2 | 48.4 |
| 7 | isodecylmethacrylate | 25.4 | 59.2 |

6

Table III-continued

| Example | Monomer | Percent Solids | Average Polymer Particle Size, Microns |
|---------|--|----------------|--|
| 8 | 60/40 weight ratio isooctylacrylate n-butylacrylate | 25.4 | 39.7 |
| 9 | 95/5 weight ratio isooctylacrylate N-t-octylacrylamide | 24.5 | 45.4 |

EXAMPLE 10

This example illustrates the use of a non-ionic surfactant and was prepared using the same equipment and techniques described in Example 1. The monomer was isooctylacrylate (500 grams). The stabilizer was a 50/50 molar ratio copolymer of acrylic acid and dimethylaminoethylmethacrylate (5 grams), and the emulsifier was "Siponic Y-500-70", tradename for an ethoxylated oleyl alcohol from Alcolac, Inc. (5 grams). The aqueous suspension of inherently tacky microspheres prepared in this manner contained 25.3 percent non-volatile material and had an average particle size of 37.4 microns.

What is claimed is:

1. Infusible, solvent-insoluble, solvent-dispersible, inherently tacky, elastomeric polymeric microspheres formed from non-ionic monomers and comprising a major portion of at least one oleophilic, water-emulsifiable alkyl acrylate or methacrylate ester, said polymeric microspheres having a glass transition temperature below about -20° C., and having been prepared by aqueous suspension polymerization in the presence of at least one anionic emulsifier at a concentration level above said emulsifier's critical micelle concentration and an ionic suspension stabilizer having an interfacial tension of at least about 15.0 dynes per centimeter.

2. The microspheres of claim 1 wherein said ester is selected from the group consisting of n-butyl acrylate, sec-butyl acrylate, 2-methyl butyl acrylate, 4-methyl-2-pentyl acrylate, 2-ethyl hexyl acrylate, isooctyl acrylate, isodecyl methacrylate.

3. The microspheres of claim 1 wherein said microspheres are homopolymers and said ester is isooctylacrylate.

4. An article comprising a substrate having disposed on at least one surface thereon infusible, solvent-insoluble, solvent-dispersible, inherently tacky, elastomeric polymeric microspheres formed from non-ionic monomers and comprising a major portion of at least one oleophilic, water-emulsifiable alkyl acrylate or methacrylate ester, said polymeric microspheres having a glass transition temperature below about -20° C., and having been prepared by aqueous suspension polymerization in the presence of at least one anionic emulsifier at a concentration level above said emulsifier's critical micelle concentration and an ionic suspension stabilizer having an interfacial tension of at least about 15.0 dynes per centimeter.

5. The article of claim 4 wherein said ester is selected from the group consisting of n-butyl acrylate, secbutyl acrylate, 2-methyl butyl acrylate, 4-methyl-2-pentyl acrylate, 2-ethyl hexyl acrylate, isooctyl acrylate, isodecyl methacrylate.

6. The article of claim 4 wherein said microspheres are homopolymers and said ester is isooctyl acrylate.

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7. A suspension polymerization process for preparing infusible, solvent-insoluble, solvent-dispersible, inherently tacky, elastomeric polymeric microspheres comprising the steps of:

(a) charging to a reaction vessel

(i) at least one alkyl acrylate or methacrylate ester monomer; and

(ii) at least one anionic emulsifier at a concentration above its critical micelle concentration; and

(iii) a substantially water-insoluble polymerization initiator; and

(iv) an ionic suspension stabilizer, having an interfacial tension of at least about 15.0 dynes per centimeter;

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(b) agitating the reaction vessel charge to create an emulsion;

(c) heating said emulsion while maintaining said agitation;

5 whereby elastomeric, solvent-dispersible polymeric microspheres are formed from said emulsion.

8. The process of claim 7 wherein said ester monomer is selected from the group consisting of n-butyl acrylate, sec-butyl acrylate, 2-methyl butyl acrylate, 4-methyl-2-pentyl acrylate, 2-ethyl hexyl acrylate, isooctyl acrylate, isodecyl methacrylate.

9. The process of claim 7 wherein said initiator is present at from about 0.15 to about 0.66 percent by weight of said monomer.

10. The process of claim 7 wherein said stabilizer is present at up to about 10 percent of said monomer.

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EXHIBITION MANAGEMENT, INC.40 WEST RIDGEWOOD AVENUE
RIDGEWOOD, NEW JERSEY 07450

Mr. Allen Amron
Press-on Memo, Ltd.
26 Middleneck Road
Great Neck, L.I., New York 11021

CT-4

NEW YORK STATE CORPORATION FRANCHISE TAX REPORT ARTICLE 9A, TAX LAW

(For corporations eligible to file this report, see instruction 1 on Page 2)

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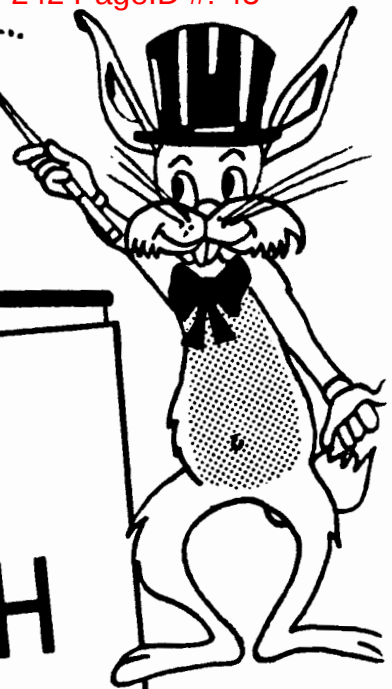


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**Actual sample of a self stick
repositionable, reusable Memo sheet
sent out in 1974 mass mailing**

United States Patent [19]

Darvell et al.

[11] **Patent Number:** 4,855,170[45] **Date of Patent:** Aug. 8, 1989

[54] **PRESSURE-SENSITIVE TAPE
CONSTRUCTION INCORPORATING
RESILIENT POLYMERIC MICROSPHERES**

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[21] **Appl. No.:** 85,239

[22] **Filed:** Aug. 13, 1987

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 898,941, Aug. 21,
1986, abandoned.

[51] **Int. Cl.⁴** B32B 5/16

[52] **U.S. Cl.** 428/40; 428/144;
428/147; 428/327; 428/343; 428/354;
428/317.5

[58] **Field of Search** 428/317.5, 147, 343,
428/40, 354, 327, 144

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Primary Examiner—Alexander S. Thomas

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[57] **ABSTRACT**

Tape products for diverse end users are obtained by applying to a sheet backing a layer of normally tacky and pressure-sensitive adhesive (PSA) containing and completely surrounding resilient non-tacky hollow thermoplastic polymeric microspheres. When the PSA is permanently bonded to the backing and the exposed surface has an irregular contour, a removable and repositionable product results. When the PSA forms a continuous matrix that is strippably bonded to the backing and is 1 mm or more thick, the resultant product is a foamlike transfer tape or foam tape. Depending on the product, the PSA can contain from about 1/5 to about 2/3% of the microspheres by volume.

24 Claims, No Drawings

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PRESSURE-SENSITIVE TAPE CONSTRUCTION INCORPORATING RESILIENT POLYMERIC MICROSPHERES

CROSS-REFERENCE TO RELATED CASES

This application is a continuation-in-part application Ser. No. 898,941, filed Aug. 21, 1986 abandoned.

BACKGROUND OF THE INVENTION

This invention relates to pressure-sensitive adhesive tapes, especially tapes which contain voids, and more particularly to tapes in which the voids are provided by incorporating hollow microspheroids. The desirability of a tape construction capable of conforming to irregular surfaces has long been recognized, one way of achieving this physical characteristic being illustrated in U.S. Pat. Nos. 3,439,950 and 4,145,465, each of which shows a foamed conformable backing coated on at least one face with a conventional pressure-sensitive adhesive (PSA). U.S. Pat. No. 3,565,247 teaches that the PSA itself may be foamed to impart conformability, U.S. Pat. No. 4,415,615 pointing out that filling the voids in the foamed adhesive with gas reduces permanent compression when the adhesive is subjected to pressure. U.S. Pat. No. 4,223,067 shows that hollow glass microspheres can be incorporated to create a foam-like appearance.

U.S. Pat. No. 3,314,838 shows the incorporation of fragile glass microbubbles at the upper surface of a PSA tape; the bubbles, which are covered with a thin coating of PSA, provide reduced adhesion and permit repositioning until the desired location is achieved, at which time the application of force crushes the bubbles and permits the main body of the adhesive to contact the surface being adhered to. Canadian Pat. No. 1,174,124, German Pat. No. 1,594,060 and U.S. Pat. No. 4,376,151 describe the incorporation of non-adhesive particles at the surface of a PSA to reduce adhesion, the particles migrating into the adhesive when sufficient pressure is applied and thereby increasing the adhesive bond.

Japanese Pat. Pubs. No. 56-61468 and 56-61469 teach the incorporation of expanded or expandable polymeric microbubbles in a pressure-sensitive adhesive. In one construction, the expanded microbubbles cover the surface of the PSA, preventing adhesion until such time as sufficient heat is applied to collapse the bubbles and expose the PSA. In the other construction, expandable microspheres are included in the pressure-sensitive adhesive, the application of heat expanding the microbubbles and destroying the bond of the PSA to a substrate to which it had been applied previously. In each case, it appears that the patentees incorporate a sufficient quantity of microspheres to constitute perhaps 90% of the total volume of the adhesive layer when the spheres are expanded, thereby effectively destroying any adhesive properties. Suitable bubbles for the patentees' purposes are taught in U.S. Pat. Nos. 3,615,972 and 4,287,308. U.S. Pat. No. 4,388,424 discloses caulk or sealant containing glass microballoons, U.S. Pat. Nos. 4,005,033 and 4,075,138 both teaching the incorporation of polymeric microspheres in the same products. Japanese Pat. Pub. No. 56-61467 suggests including unexpanded plas-

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tic bubbles in adhesives (including PSAs), interposing the adhesive between two objects to be bonded and applying heat to expand the bubbles and fill gaps between the objects. U.S. Pat. No. 3,864,161 describes the incorporation of 0.25 to 40% by weight unexpanded hollow polymeric microspheres in a solution of a film-forming coating of adhesive polymer, coating the composition on a substrate, drying, and heating to expand the microspheres and form foam-like products (either open or closed cell) that are suggested for decorative coatings, padding, and gaskets.

U.S. Pat. Nos. 3,691,140 and 4,166,152 describe inherently tacky microspheres, which in U.S. Pat. Nos. 4,049,483 and 3,857,731 are used in conjunction with other adhesives, allowing the microspheres to protrude above the surface and thereby provide an adhesion level lower than if the adhesive surface were uniform and smooth; products in which inherently tacky microspheres are bonded to a paper backing are sold by Minnesota Mining and Manufacturing Company as "POST-IT" Brand notes, which can be repeatedly applied to paper, removed, and replaced without delaminating the paper. U.S. Pat. No. 4,588,152 discloses the use of small spaced pressure-sensitive adhesive areas which are said to provide a repositionable tape product.

Alternative approaches to the development of a removable and repositionable pressure-sensitive sheet of this type have included modifying conventional pressure-sensitive adhesives (PSAs) by lowering the initial adhesion and attempting to minimize the subsequent adhesion buildup which occurs as the adhesive remains in contact with the substrate, employing firmer adhesives, minimizing cold flow, and decreasing the total surface area coated with adhesive. Although successful to some extent, each of these techniques is limited in its ability to provide a balance of properties, i.e., sufficient adhesion to ensure attachment while minimizing the ultimate adhesion buildup so as to permit removal. The present invention provides a means of achieving all the advantages of prior art while avoiding the disadvantages. Conventional PSAs can be employed, while avoiding any adhesive transfer, maintaining removability over extended periods, and retaining excellent shear properties.

Another widely used commercial product is so-called "foam tape", in which a foam backing is provided on each face with a coating of PSA. For foam-like tapes, photopolymerizable or thermally polymerizable monomer systems are particularly preferred. These systems preferably comprise one or more monomers that are predominantly alkyl acrylate, the alkyl groups of which have an average of 4 to 12 carbon atoms, and a minor proportion of one or more polar co-polymerizable monomers such as disclosed in U.S. Pat. No. 2,884,126. Tapes of this type are, for example, especially effective in mounting resilient molding to the sides of automobiles to prevent inadvertent damage to the finish. In some cases, the foam backing is replaced with an adhesive that contains glass microbubbles to create a pseudo-foam effect while simultaneously retaining the adhesive properties of the PSA. The latter construction can be

modified by laminating an unfoamed PSA to one or both faces. While effective in most circumstances, products of all these types are sensitive to shock at extremely low temperatures.

BRIEF SUMMARY

The present invention provides an improved family of pressure-sensitive adhesive tape products, including repositionable adhesive-coated sheets, transfer tapes having the same or different adhesive characteristics on opposite faces, compressible tape products resistant to shock at extremely cold temperatures, as well as a wide variety of other products. Tape constructions made in accordance with the invention may be tailored to control adhesion, conformability, and certain other properties as well as to improve static shear, internal strength, tensile strength, shock resistance and humidity resistance.

Diverse products of the types just described may be characterized as pressure-sensitive adhesive-coated sheet material comprising in combination a sheet backing bearing on at least one surface a layer of normally tacky and pressure-sensitive adhesive on the order of at least 20 micrometers thick, this adhesive layer containing up to about $\frac{2}{3}$ by volume of resilient non-tacky hollow thermoplastic polymeric spheres, especially vinylidene chloride:acrylonitrile copolymer spheres, having a diameter in the approximate range of 10–125 micrometers, preferably at least about $\frac{1}{3}$ of the spheres having a diameter in the range of 30–70 micrometers. All of the copolymer spheres are substantially completely surrounded by the pressure-sensitive adhesive and thus always present an adhesive surface, distinguishing the products of the invention from those described in the aforementioned Japanese Pat. Pubs. No. 56-61467, 56-61468, 56-61469.

When the adhesive layer is permanently bonded to the backing and the exposed surface of the adhesive layer has an irregular contour caused by the presence of the hollow polymeric spheres, the resultant sheet material can be repeatedly adhered to paper substrates and removed without tearing the paper. Such products are capable of substantially complete recovery after being subjected to a compressive pressure of 80 kPa. On the other hand, when the adhesive layer forms a continuous matrix that is strippably bonded to the backing and is on the order of one millimeter thick, the resultant foamlike transfer tape is suited, e.g., for mounting molding strips on automobiles, dispensers on walls, mirrors on vertical surfaces, and flexographic printing plates on steel cylinders.

In principle, the specific type of pressure-sensitive adhesive employed in carrying out the invention is not critical. Thus, the adhesive can be of the rubber-resin type, the "rubber" being natural or synthetic rubber, including block copolymers. It is sometimes preferred, however, to employ the so-called "acrylate" adhesives, which not only are less prone to discoloration than the rubber-resin types but also are capable of rather precise control during preparation; see, e.g., U.S. Pat. No. 2,884,126.

The hollow polymeric spheres employed are typically of the type disclosed in U.S. Pat. No. 3,615,972,

which describes various vinyl polymers containing a hydrocarbon liquid that volatilizes at a temperature slightly below the softening point of the polymeric spheres. Thus, a sphere that is originally on the order of 10 micrometers in diameter, when heated to a temperature of, e.g., 120° C., is expanded to an average diameter of e.g., 30–60 micrometers. It is possible to include the unexpanded microspheres in the PSA and substantially heat them to effect expansion, but it is generally preferred to mix the expanded microspheres directly into the adhesive, a process which makes it easier to ensure that the hollow microspheres in the final adhesive are substantially completely surrounded by at least a thin layer of PSA.

The polymeric microspheres mentioned can be added to an adhesive system after the adhesive matrix has been polymerized; it is also possible and sometimes desirable, however, to add them to an adhesive monomer system prior to polymerization. The latter procedure is especially preferred for making a foam-like tape.

As previously indicated, hollow elastomeric, resilient polymeric microspheres are used in the practice of this invention. Such microspheres and their methods of preparation are described in U.S. Pat. Nos. 3,615,972, 4,075,138, and 4,287,308. The microspheres are available from the Pierce & Stevens Company under the trade name "Microlite" in unexpanded form and "Miralite" in expanded form. Similar microspheres are available from Kema Nord Plastics under the trade name "Expancel", from Matsomoto Yushi Seiyaku under the trade name "Micropearl", and formerly from Dow Chemical Company under the trade name "Saran". In expanded form the microspheres have a specific density of approximately 0.01–0.04 g/cm, typically 0.02–0.036 g/cc. Perhaps because of the thin, flexible shells of such microspheres (on the order of 0.02 micrometer according to trade literature), their rough surface, or their organic nature, they appear to be mechanically and/or chemically bonded to PSAs in which they are incorporated, becoming almost an integral part of the adhesive mass, distorting when the mass is subjected to pressures, distributing stress, absorbing energy, and exhibiting distinctly different characteristics from otherwise identical adhesive compositions incorporating only hollow glass or other rigid microspheres.

Addition of polymeric microspheres to an adhesive system prior to polymerization seems to enhance this behavior, the resultant tape (such as a foam-like tape) having a unique combination of superior low temperature performance and such desirable mechanical properties as superior compression recovery, high peel strength, improved static shear, and high tensile strength.

Fundamental methods of dynamic mechanical analysis (DMA), particularly when utilized in concert with more common techniques for analysis (e.g., ASTM tests), offer great potential to enhance understanding of structure/property relationships for adhesive systems. Dynamic mechanical analyses characterize the response of an adhesive to an applied stress as a function of either

frequency or temperature (with the remaining parameter fixed). Response to stress is quantified in terms of a storage modulus (G') and a loss modulus (G''). The correlation of these two moduli is fundamental for characterization of a PSA system, and is increasingly instrumental in the design of new generation adhesives.

It has been established that incorporation of voids such as gas bubbles or rigid (e.g., glass) microspheres in an adhesive matrix modifies the morphological and rheological characteristics of the system in generally predictable ways.

In contrast, results of dynamic mechanical analyses and the more commonly applied physical and mechanical property tests, correlate well to demonstrate that incorporation of resilient polymeric microspheres modifies both surface and bulk properties of the adhesive in ways not previously predicted, observed or utilized. DMA results indicate that the flexible polymeric bubbles impart a means for energy and/or stress dissipation not present in unfilled systems, or in systems containing either gas-filled voids or hollow glass microspheres. Consistent with these results, established physical and mechanical property tests demonstrate that the plastic bubble-filled adhesive tapes of the present invention exhibit an outstanding balance of properties with regard to low temperature shock performance, internal strength, conformability and recoverable compressibility. This range of performance is greatly superior to any previously known PSA tape construction.

The novel behavior apparently arises from the union of the appropriate polymer matrix intimately incorporating thin-walled flexible microbubbles that are responsive to deformation resulting from stress(es) imposed on the polymer matrix. The overall surface and bulk properties of the composite will depend on the concentration and distribution of the microbubbles (i.e., homogeneous or asymmetric, such as increased concentration near the adhesive surface).

The present invention thus provides a means for tailoring a family of adhesive constructions that exhibit specified initial adhesion, controlled adhesion build, shear strength, recoverable compressibility and if desired, differential adhesion.

The bulk adhesive viscoelastic properties, as measured by dynamic mechanical thermal analysis (DMTA), as detailed in ASTM Test Procedure D4065-2, demonstrate that the addition of resilient polymeric particles to the adhesive results in a more elastic material over the temperature range of 0°-120° C. For example, at room temperature (25° C.), the shear storage modulus, G' , at 10 Hz for the base adhesive (IOA:AA) is 9.3×10^5 dynes/cm², which is a typical value for a PSA. The corresponding modulus for the same adhesive with the addition of 6.8 phr polymeric spheres is 1.3×10^7 dynes/cm², representing a more elastic material.

The adhesive/particle composites resist cold flow (and the resultant increase in adhesion) that normally occurs gradually when an adhesive remains in contact with a substrate for extended periods. The exact effect

achieved varies with the type of adhesive and the polymeric microsphere content.

Dynamic mechanical analysis (DMA) may be used to simulate the creep/recovery cycle that an adhesive will experience in actual use. A refined description of DMA techniques especially suited for use with PSAs appears in "Evaluation of the Role of Microphase Separation in Adhesion," the doctoral dissertation of Margaret M. Sheridan, submitted to Virginia Polytechnic Institute and State University, Blacksburg, Va., in August, 1985. When tested in accordance with DMA procedures, homogeneous PSAs are characterized by a high degree of compliance but a low degree of recovery. When such PSAs are modified by incorporating polymeric microspheres, however, not only is compliance increased (as is evidenced by increased penetration or compressive creep while the force is applied), but there is also a substantially greater recovery to the original dimensions after the compressive force is removed. In general, the degree of penetration is directly related to the volume concentration of the hollow polymeric spheres until the concentration approaches close pack volume. In actual use, the initial bond formation of a PSA is directly related to the extent of penetration determined by DMA techniques.

In contrast to the effect achieved by incorporating hollow polymeric microspheres in a homogeneous PSA, the incorporation of rigid particles (e.g., glass microbubbles) decreases both compliance and recovery.

The modified properties of the adhesive composite appear to be due to a combination of the changed bulk adhesive viscoelastic properties and the altered topological effects that result from the addition of the polymeric spheres. Peel adhesion, shear, and other properties of the selected base polymer can be controllably altered by varying the volume percentage of particles. For example, in a foam-like adhesive tape such as that used for permanent mounting of molding strips on automobiles, the volume loading of polymeric microspheres in the adhesive matrix is preferably from 1/5 to 1/2, more preferably 3/10 to 2/5, and the microspheres are preferably added to the monomer system prior to polymerization in order to achieve the unique combination of properties previously mentioned. At a volume loading of less than 1/5, the tape properties are similar to those of the parent polymer matrix, and so the desired properties are not optimized. On the other hand, a volume loading of greater than 1/2 results in diminished tensile strength, internal strength and 90° peel adhesion.

Adhesives made in accordance with the invention may, of course, also include conventional additives such as dyes, pigments, fumed silica, chopped fibers, hollow glass microspheres, fillers, catalysts, crosslinking agents, and the like to achieve specific effects. Similarly, separately formed microbubble-free PSA layers can be laminated to one or both surfaces of a PSA layer containing polymeric microbubbles.

Several tests have been found helpful in evaluating the performance of tapes made in accordance with the invention. Details of these tests are provided below:

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90° Peel Adhesion

A strip of 25-micrometer polyester film, 31.75 mm wide, is positioned on the adhesive side of the sample. Pressure is applied to the polyester strip by rolling it twice with a 2-kg roller. The opposite face of the sample is then firmly bonded to a rigid substrate and the polyester strip removed at 90° to the adhesive surface at a speed of 30.5 cm/minute, noting the average adhesion in g/cm width.

By incorporating varying amounts of hollow polymeric microspheres into a pressure-sensitive adhesive, one can obtain peel adhesion values ranging from that obtainable with microsphere-free adhesive to zero, by increments proportional to the volume of spheres added.

180° Peel Adhesion

A stainless steel (AISI 302 or 304) test panel at least 50×125 mm, is obtained and the 25 mm immediately joining the lower edge covered with masking tape. Two 100 mm strips of adhesive transfer tape or adhesive foam tape, carried on a removable liner, are adhered, side by side, to the exposed portion of the stainless steel panel. The liner is then removed and a 300 mm strip of 25 mm wide×25 micrometer thick polyester film is placed in contact with the exposed adhesive so as to extend beyond the transfer tape on the edge covered with the masking tape. The tape is rolled down using a 2-kg roller at the rate of 300 mm/minute, once in each direction, and the sample allowed to dwell for 20 minutes. The polyester is then doubled back on itself and the masking tape-covered edge of the panel is clamped in the lower jaw of a tensile tester, the polyester doubled back on itself and clamped in the upper jaw of the tensile tester, and the jaws separated at a rate of 300 mm/minute, noting the average adhesion value. Further details of this test are set forth in "Test Methods for Pressure-Sensitive Tapes", Pressure-Sensitive Tape Council, Glenview, IL, 9th Edition, as PSTC-3.

Breakaway/Continuous Peel

A 12.7 mm×200 mm adhesive foam tape, carried on a release liner, is aligned squarely over the 15 mm×150 mm face of a rigid poly(vinyl chloride) test bar about 6 mm thick and pressed firmly into place by rolling once with a 6.8-kg roller. The liner is then removed from the tape and the exposed adhesive surface aligned in the center of a freshly painted steel panel approximately 100 mm×300 mm, with one end of the test bar extending beyond the end of the panels, rolling the test bar with the 6.8-kg roller at the rate of about 300 mm/minute to ensure good contact. The specimen is then allowed to age for any desired period of time, after which a metal shear is used to trim the width of the panel to approximately 50 mm. The specimen is then clamped in a horizontal fixture mounted in the lower jaw of a tensile testing machine. A metal bar approximately 8 mm thick and having an opening at one end corresponding to the cross section of the vinyl test bar is slipped over the extended end of the test bar and the opposite end gripped in the upper jaw of the tensile testing machine. The jaws are then separated at 30.5 cm/minute, noting

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both the force required to initiate separation of the vinyl test bar from the painted panel and the force required to continue the separation until the bar is completely removed.

Cold Slam

A rigid vertical frame approximately 40 cm square is provided at its upper edge with similarly dimensioned hinged frame. Silicone foam shock absorbing tape is then mounted at five locations on the vertical frame. A 100 mm×300 mm steel test panel on which four 15 mm vinyl test bars (of the type described in the preceding test) are mounted within the hinged frame and allowed to remain 72 hours at room temperature. The assembly is then placed in a -30° C. cold room for 16 hours and immediately subjected to a test in which the hinged portion of the frame is raised to a horizontal position and allowed to drop, slamming against the vertical portion, noting whether any of the vinyl test bars become detached. After 10 slams, the test is deemed completed and the number of failures is reported.

Static Shear Test

A strip of 12.7 mm wide transfer tape or double-coated tape, carried on a strippable liner, is adhered to one end of a stainless steel test panel and trimmed to a length of 25.4 mm. The liner is then removed and a second stainless steel panel adhered to the exposed adhesive surface. The specimen is placed in a horizontal position and a 1-kg weight applied for a period of 15 minutes to ensure intimate contact between the surfaces. The assembly is then mounted in a vertical plane, suspended from the upper edge of one panel and a weight of the desired size attached to the lower edge of the other panel. The time before the panel to which the weight is attached falls is noted. If no failure occurs, the test is discontinued after 10,000 minutes. Further details of this test may be found in the aforementioned "Test Methods for Pressure-Sensitive Tapes", as PSTC-7.

Tensile Elongation

A dumbbell-shaped strip of a tape to be tested is prepared, and each end wrapped with 42-mm wide cellophane tape, leaving a 50mm33 6.4-mm strip of the test tape exposed. The cellophane-covered ends of the test specimen are then clamped in the opposite jaws of a tensile machine, and the jaws separated at a rate of 500 mm/minute, recording the elongation at break and calculating the tensile strength, based on the thickness of the test tape.

T-Peel

A foam tape or other double-coated tape sample is placed between two strips of 25 mm×200 mm×0.125 mm anodized aluminum, leaving an adhesive-free 25 mm tab at each end of each aluminum strip. The assembly is rolled down with a 6.8 kg roller, one pass in each direction, and the samples then conditioned for 1-2 hours at room temperature. The tabs are bent back at 90° in opposite directions and respectively clamped in the upper and lower jaws of a tensile testing machine,

after which the jaws are separated at 30 mm/minute, noting the average force required to effect separation.

Performance Aging

Adhesive sample strips, 2.54 cm wide, are applied to a bleached white xerographic paper weighing 78 g/m² and secured by rolling four times with a 2-kg roller. The sample strip is then removed at 90° to the paper surface, at a rate of 30.5 cm/minute, noting the initial average adhesion in g/cm width.

A duplicate adhesive sample, attached to the same bond paper, is aged at 50° C. for 14 days. After the laminate has adjusted to room temperature, the sample strip is removed, as above. The adhesion is noted and the sample is inspected for delamination and adhesive residue. The force to separate the adhesive-coated substrate from a bond paper, after 14 days aging, is used as a criterion to select optimum formulations. Generally, such formulations yield adhesive samples having enough surface roughness that appreciably less than 100% contact is maintained with the paper surface. Scanning electron micrographs of the peel interface have shown that "stranding" of the adhesive occurs in a manner similar to that which takes place with the microsphere adhesive of "POST-IT" Brand Notes, perhaps contributing to the uniformity of the force required to peel the adhesive continuously away from a substrate.

It is evident that the internal mechanical properties of the adhesive are altered by the inclusion of the polymeric particles. Throughout the temperature range of 0°-120° C., the elastic modulus of a PSA is greater when hollow polymeric microspheres are incorporated than when they are not, the increase being directly related to the concentration of microspheres. The cold flow decreases, retarding the increase in adhesion that normally occurs gradually when an adhesive remains in contact with a substrate for extended periods.

Although the peel adhesion of a homogeneous PSA can be substantially reduced by incorporating hollow polymeric microspheres, the shear holding power is only slightly reduced. To illustrate, while the peel adhesion of a given adhesive is reduced from 190 g/cm to 15.75 g/cm, the shear values are reduced from 3.31 kPa only to 2.34 kPa. As a reference, "POST-IT" Brand Notes typically have a peel adhesion of 28 g/cm and a shear value of 0.76 kPa. Improved shear holding power appears to be due in part, to the enhanced conformability of a PSA incorporating polymeric microspheres as evidenced by dynamic mechanical analysis. Thick composite PSA layers, having a continuous adhesive matrix, not only maintain desirable high peel adhesion values but also demonstrate enhanced conformability and shear holding power.

Dynamic Shear

A 2.54 cm×2.54 cm adhesive sample is attached to a clean stainless steel test panel and pressure applied by rolling 4 times with a 2-kg roller. A shear force is applied at 0° to the surface of the sample at a rate of 1.27 cm/minute, noting the maximum force to rupture the adhesive bond, expressed in N/cm².

The invention will now be described with the aid of illustrative but nonlimitative examples, in which all parts and percentages are by weight unless otherwise noted.

EXAMPLE 1

100 parts of a 55% solids aqueous emulsion of a proprietary modified isooctyl-acrylate: acrylic acid copolymer, of the type disclosed in Ulrich U.S. Pat. No. Re. 24,906, was blended with 8 parts of "Miralite 177" expanded vinylidene chloride:acrylonitrile copolymer microspheres having an average diameter of approximately 40 micrometers. The blend was knife-coated at a thickness of 50 micrometers onto the surface of a 40-micrometer cellulose acetate film and dried in a circulating air oven at 100° C., leaving an adhesive containing 63% microspheres by volume. As the water evaporated during the drying process, the adhesive tended to drain down, leaving an irregular surface occupied by the microspheres, a thin layer of adhesive continuing to cover the microspheres, however, in all cases. When the resultant adhesive-coated film was applied to bond paper and a squeegee used to ensure uniform contact, the film could be removed without delaminating the paper. A second adhesive was made in the same way except that 100 parts of the acrylate adhesive emulsion was blended with 50 parts of the "Miralite 177" microspheres; after drying, the adhesive coating contained only 30% microspheres by volume. When this composite adhesive was coated on cellulose acetate film and applied to bond paper, the resultant tape-like product could not be removed without delaminating the paper, apparently because there was sufficient space between the microspheres to permit a substantial area of the flat adhesive surface to come into intimate contact with the bond paper.

EXAMPLE 2

100 parts of the acrylate emulsion adhesive of Example 1 was blended with 4.4 parts of "Miralite" 177 polymeric microspheres. The composition was then knife-coated at a 76-micrometer orifice onto bond paper weighing 75 g/m² and having a thickness of 100 micrometers. The adhesive-coated paper was dried at 100° C., the resultant adhesive containing 67% hollow microspheres by volume, after which it was found to be removable from the bond paper substrate, exhibiting a peel adhesion of 18.9 g/cm width. Sheets were cut from the adhesive-coated paper and manually stacked to form a pad of notes, which was then trimmed to size with a guillotine knife. After one year of aging, individual sheets were removed from the pad and found to exhibit an adhesion to polyester film of 25.2 g/cm width. Adhesive-coated sheets prepared in the same way, except that no microspheres were included in the adhesive, would ordinarily be expected to exhibit a peel adhesion of approximately 250 g/cm width.

EXAMPLE 3

100 parts of a 42% solids aqueous emulsion of 95:5 isooctyl acrylate:acrylic acid copolymer was blended with 4.5 parts of a 50% solids aqueous slurry of "Micro-

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lite" 101 unexpanded polymeric microspheres, using a high speed blender to obtain a uniform dispersion. The dispersion was allowed to stand for 24 hours to permit entrapped air to escape, and the spheres were then resuspended by simple stirring. Using a knife coater having a 76-micrometer orifice, the dispersion was coated on 76-micrometer polyester film that had first been primed with a polycarbodiimide. The adhesive-coated film was then dried in a conventional air circulating oven for 3 minutes at 100° C., a temperature adequate to expand the microspheres from their initial average diameter of approximately 10 micrometers to approximately 40 micrometers and yield an adhesive containing 60% hollow microspheres by volume. It has been found highly desirable to permit the adhesive to dry partially but not completely, leaving a somewhat "skinned over" surface, before expanding the microspheres. If the adhesive is permitted to dry completely, expansion of the microspheres can result in a greater number protruding above the adhesive matrix, having no adhesive covering. For purposes of the present invention, it is essential that substantially all of the expanded microspheres be completely surrounded by adhesive.

The product of this Example 3 was allowed to adjust to room temperature, after which the initial peel adhesion to polyester film was measured and found to be 40 g/cm width. Peel adhesion for the same adhesive, but containing no microspheres, was approximately 190 g/cm width. When the product of this example was applied to bond paper, the force required to remove it after 14 days was 43 g/cm width.

Although one contemplated use for adhesives like that of the present example is in the preparation of removable tape products functionally equivalent to 3M's "POST-IT" Brand notes, which are frequently applied to paper substrates, it has been found that measurements of adhesion to paper are somewhat erratic, paper itself not being a consistent product. Accordingly, more precise peel adhesion figures may be obtained by applying the adhesive to a polyester film substrate.

EXAMPLE 4

100 parts of a 55% solid aqueous emulsion of a proprietary modified isooctylacrylate: acrylic acid copolymer, of the type disclosed in Ulrich U.S. Pat. No. Re. 24,906, was blended with 6 parts of "Microlite 126", unexpanded terpolymeric microspheres (average diameter about 7-15 micrometers) formed from poly(vinylidene chloride), acrylonitrile and a proprietary monomer, believed to be methylacrylate. The dispersion was coated using a knife orifice of 50 micrometers on 76-micrometer polyester film. The sample was allowed to air dry, after which microscopic examination showed that the microspheres were embedded in the layer of adhesive. The sample was then subjected to a temperature of 150° C., slightly above the recommended temperature of 140°-145° C. recommended for efficient expansion. Microscopic examination showed that the microspheres had expanded to an average diameter of about 30 micrometers. The adhesive composite was readily removable from bond paper after being rolled twice with a 2-kg roller.

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EXAMPLE 5

100 parts of a 39% solids aqueous emulsion of a 95:5 isooctylacrylate:acrylic acid copolymer PSA and 2.2 parts "Miralite" 177 expanded polymeric microspheres were mixed together. When the dispersion was coated as described in Example 3 and dried (at a somewhat lower temperature since the microspheres had previously been expanded), a tape product was obtained in which the PSA contained 61% hollow microspheres by volume and the tape had an average initial peel adhesion of 41.9 g/cm when applied to polyester film. When the product was applied to bond paper, the force required to effect removal after 14 days was 37.4 g/cm width.

EXAMPLE 6

100 parts of a 20% solids solution of a 95.5:4.5 isooctylacrylate:acrylic acid copolymer in methyl isobutylketone was blended with 0.71 part "Miralite" 177 expanded polymer microspheres. The procedure of Example 4 was followed, except that the more dilute adhesive was coated at a thickness of 102 micrometers. After drying, the adhesive coating contained 50% hollow microspheres by volume. Initial peel adhesion to polyester film was 30.2 g/cm, and the force required to remove the product from bond paper after 14 days was 27.6 g/cm width.

EXAMPLE 7

40.9 parts of a 61.9% solids natural rubber latex ("Hartex" 103, available from Firestone Rubber Company), was mixed with 47.2 parts of a 55.7% solids aqueous dispersion of tackifier resin ("Foral" 85-55, available from Hercules, Inc.), 2.5 parts "Miralite" 177 polymeric microspheres, and 16.1 parts water were mixed together. Following the procedure of Example 5, the adhesive dispersion was coated on polyester film that had been primed with a 7.5% solids solution of 1:1 butadiene-acrylonitrile:butadiene-styrene rubber ("Hy-car-GRS") in a 1:1 toluene:methyl ethyl ketone solvent blend, the dried adhesive containing 60% hollow microspheres by volume. The initial peel adhesion to polyester film was 44.7 g/cm width, and the force required to effect removal from bond paper after 14 days was 53.1 g/cm. In the absence of polymeric microspheres, the peel adhesion to polyester film was 127.6 g/cm width.

EXAMPLE 8

100 parts of a 42% solids aqueous dispersion of a 95:5 isooctylacrylate:acrylic acid copolymer was mixed with 3.5 parts of a 50% solids aqueous slurry of "Microlite" 101 unexpanded polymeric microbubbles. The adhesive was sprayed onto bond paper weighing 75 g/m² and dried at 100° C. to expand the microspheres, the dried adhesive containing 54% hollow microspheres by volume. Initial adhesion to polyester film was on the order of 25 g/cm width.

EXAMPLES 9-12

A series of adhesive dispersions was prepared by adding incremental amounts of "Miralite" 177 expanded polymeric microbubbles to separate 100-part aliquots of

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a 42% solid aqueous emulsion of a 95:5 isooctylacrylate:acrylic acid copolymer. The procedure of Example 5 was then followed except that a 0.5-mm coat of each adhesive was applied to a silicone-coated release liner ("Shiny 164", available from Daubert). The resultant products were transferable PSA coatings (i.e., transfer tapes) in which the peel adhesion of the upper (exposed) adhesive surface was lower than that of the adhesive surface in contact with the liner; the differential adhesion was attributable to the fact that, the exposed surface was more irregular, because of the presence of the microspheres. Results are tabulated below:

TABLE I

| Ex. | Parts "Miralite" 177 by weight | Percent Microspheres by volume | 90° Peel adhesion, upper surface, g/cm width | 90° Peel adhesion, lower surface, g/cm width |
|-----|---|--------------------------------------|--|--|
| 9 | 1.6 | 55 | 42.5 | 283 |
| 10 | 2.4 | 64 | 33.1 | 135 |
| 11 | 3.2 | 71 | 28.3 | 83.5 |
| 12 | 4.0 | 75 | 28.3 | 40.9 |

Several 3.8 cm×3.8 cm squares of the transfer tape of Example 9, carried on the release liner, were die-cut and evaluated further. The exposed surface of two of these squares was then adhered to the back of a sheet of easel

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EXAMPLE 14

A product was prepared as in Example 13 except that a nonwoven web weighing 18.75 g/m² was sandwiched between the two adhesive surfaces. Handling, dimensional stability, and dispensability were all improved. If desired, a first homogeneous PSA may be applied to one face and a second homogeneous PSA, incompatible with the first (cf. U.S. Pat. No. 2,889,038) applied to the other face, resulting in a reinforced foam tape that can be wound convolutely directly on itself to form a roll and subsequently unwound. In a variation of Example 14, one of the two transfer tapes may be omitted and nonwoven fabric, scrim, etc., adhered only to the other transfer tape, resulting in a reinforced tape structure having adhesive on only one face.

EXAMPLES 15-20

A series of aqueous dispersions was formulated by adding incremental amounts of "Miralite" 177 expanded polymeric microspheres to separate 100 pbw aliquots of a 37% solids aqueous dispersion of 95:5 isooctylacrylate:acrylic acid copolymer. Each dispersion was then coated on a 75-micrometer polyester film backing, dried, and tested, obtaining the results summarized below:

TABLE II

| Example | Parts polymeric microspheres by weight | Percent microspheres by volume | Initial adhesion to polyester film, g/cm width | Initial adhesion to bond paper, g/cm width | Adhesion to bond paper after 14 days at 49° C., g/cm width | Initial room temperature shear holding power, kg/cm ² |
|-----------------|---|--------------------------------------|--|---|--|---|
| 15 (Control) | 0 | 0 | 181 | Delaminated | Delaminated | 3.34 |
| 16 | 0.8 | 38 | 109 | 37.4 | 88.6 | 2.62 |
| 17 | 1.6 | 55 | 52.0 | 31.5 | 80.7 | 1.98 |
| 18 | 2.4 | 64 | 43.8 | 27.6 | 70.9 | 2.43 |
| 19 | 3.2 | 71 | 23.9 | 19.7 | 39.4 | 2.43 |
| 20 | 4.0 | 75 | 18.3 | 9.8 | 27.6 | 2.40 |

paper, other pairs being similarly adhered to two other sheets of the same easel paper. The liners were then removed and the sheets adhered, respectively to a painted cinder block wall, a painted wall board surface, and a glass surface. After a dwell time of 35 days, the adhesive was readily removed from each of the substrates. With care, the adhesive squares on the back of the easel paper could be rolled up and removed. Substantially the same results can be obtained with much thicker adhesive coatings, e.g., 4 mm. Such products possess the unusual combination of low peel strength, much lower than for conventional homogeneous PSAs, but shear strength nearly equal to that of such adhesives. Thick adhesive layers of this type thus permit ready attachment to even irregular substrates while still affording easy removal.

EXAMPLE 13

The release liner was removed from each of two transfer tapes prepared as in Example 10 and the two newly exposed adhesive surfaces placed in contact with each other. The resultant product had twice the thickness of the Example 10 product but was somewhat more difficult to tear or dispense.

The foregoing examples show that peel adhesion is gradually decreased as the percent microspheres by volume is increased, while the shear holding power remains relatively constant.

EXAMPLES 21-24

A 91:9 isooctylacrylate:acrylic acid blend was partially thermally polymerized (8% conversion) to yield a syrup. To each of four 100 g aliquots of this syrup was added 0.08 g 1,6-hexanediol diacrylate (HDDA) cross-linker, 0.15 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) photoinitiator, and 4.0 g hydrophobic fumed silica ("Aerosil" R-972). To the Example 21 aliquot, which serves as a control, was added 8.0 g glass microbubbles averaging 55 micrometers in diameter, having a specific gravity of 0.15. To each of the compositions of Examples 22, 23, and 24 was added 2.15 g of polymeric microspheres having, respectively, number average diameters of 12 micrometers ("Expancel" 551DE20), 23 micrometers ("Expancel" 551DE), and 50 micrometers ("Expancel" 461DE). Each sample was thoroughly mixed using a propeller stirrer, degassed in a desiccator, and polymerized between two silicone-coated polyester film liners, using 410 mJ/cm² of fluo-

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rescent black light to effect curing. In each case, the thickness of the cured adhesive layer was 800 micrometers, the hollow polymer microsphere content was 32.3% by volume, and the adhesive was a crosslinked acrylate PSA. A number of tests were then performed on each of the adhesives, with results as shown below:

TABLE III

| Test | Example | | | |
|---|---------|-------|---------|---------|
| | Control | 21 | 22 | 23 |
| Tensile strength, N/mm ² | 0.81 | 1.16 | 1.16 | 1.18 |
| Elongation at break, % | 924 | 1,007 | 942 | 889 |
| T-Peel, N/cm | 25.6 | 28.0 | 29.1 | 28.3 |
| High temperature static shear (70° C., 1250 g wt), minutes to failure | 190 | 1,200 | 10,000+ | 10,000+ |

Several observations can be made with respect to the foregoing examples. Independent of the particle size, compared to the PSA filled with glass microbubbles, PSAs filled with polymeric microbubbles showed approximately 30% increase in tensile strength and 10-15% increase in internal strength. All three examples containing polymeric microspheres were significantly more resistant to high temperature static shear than the glass microbubble-filled adhesive tape.

When the tapes of Examples 21-24 were adhered to a steel panel painted with automotive enamel (Ford 50J107A) the force required to initiate and continue removal was measured after various lengths of time, with results as shown below:

TABLE IV

| Dwell time | Environmental conditions of dwell | Force required to initiate removal, N/cm, after dwell indicated | | | |
|------------|-----------------------------------|---|-------|---------|-------|
| | | Control | | Example | |
| | | 21 | 22 | 23 | 24 |
| 2 minutes | room temperature | 96.1 | 126.8 | 124.4 | 115.7 |
| 72 hours | room temperature | 133.9 | 163.8 | 162.2 | 133.1 |
| 72 hours | 38° C., 100% RH | 90.6 | 135.4 | 133.1 | 129.1 |

TABLE V

| Dwell time | Environmental conditions of dwell | Force to continue peel, N/cm width | | | |
|------------|-----------------------------------|------------------------------------|------|---------|------|
| | | Control | | Example | |
| | | 21 | 22 | 23 | 24 |
| 2 minutes | room temperature | 13.4 | 15.7 | 18.9 | 17.3 |
| 72 hours | room temperature | 59.1 | 63.8 | 57.5 | 40.2 |
| 72 hours | 38° C., 100% RH | 48.0 | 51.2 | 52.8 | 59.1 |

In all tests conducted after a 2-minute dwell time, the adhesive popped off the painted panel; in all other tests, the adhesive split during removal. The superiority of the polymeric microsphere-filled adhesive to the glass microbubble-filled adhesives was apparent.

The products of control Example 21 and experimental Example 23 were then compared for their resistance to cold temperature. In the "cold slam test", where four specimens were mounted on a painted panel, two of control Example 21 specimens popped off during the first slam and the other two during the second; in con-

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trast, the product of Example 23 showed no failures after ten slams.

The superiority of Example 23 product to commercial products containing glass microbubbles was also demonstrated under such extreme conditions as aging for 4 weeks at 90° C.; undergoing 4 complete cycles of 8 hours at -35° C., 16 hours at 38° C. and 100% relative humidity, and 8 hours at 70° C.; 7 days at 70° C. and 100% condensing humidity followed by 24 hours at -30° C. and 4 hours conditioning to room temperature.

EXAMPLES 25-27

A tackified rubber-resin adhesive was prepared by dissolving 21.3 parts 15:85 styrene:isoprene block copolymer ("Cariflex" 1107), 28.7 parts petroleum-based synthetic resin tackifier (available from Enjay Chemical Co. as "Escorez" 1310), 14.5 parts pinene palmyrate (available from Arizona Chemicals as "Zonarez" A-25) and 0.5 part octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate antioxidant (available from Ciba Geigy as "Irganox" 1076) in 35 parts of a 77:23 toluene:heptane solvent. The adhesive was then divided into three aliquot parts, one of which was employed as a control, with no polymeric microspheres included, and the other two of which had different amounts of polymeric microspheres included. In each case, the adhesive was knife-coated on a silicone-treated paper backing, dried 5 minutes at room temperature, placed in a 70° C. forced air oven for 10 minutes, removed, and allowed to adjust to room temperature. Both surfaces of the control (Example 25) appeared smooth, as did the surfaces of Examples 26 and 27 that had been in contact with the liner; the exposed surfaces of the latter two adhesive layers, although relatively smooth, were less smooth than the surfaces that had been in contact with the liner. The 180° peel adhesion to each surface was then determined, the pertinent data being tabulated below:

TABLE VI

| Example | Parts "Expancel" DE/100 parts adhesive | Percent "Expancel" by volume | Dried thickness, micro-meters | Adhesion, N/cm | |
|--------------|--|------------------------------|-------------------------------|----------------|--------------|
| | | | | Liner side | Exposed side |
| 25 (Control) | 0 | 0 | 75 | 15.0 | 13.8 |
| 26 | 0.7 | 36 | 59 | 10.2 | 8.7 |
| 27 | 1.5 | 48 | 64 | 8.7 | 7.1 |

The difference in peel adhesion values between the two surfaces depends to a considerable extent upon the viscosity of the adhesive. Adhesives having a lower viscosity than those of Examples 25-27 permit a greater migration of the bubbles to the exposed surface, thereby reducing the adhesive surface available for contacting a substrate and, as a result, reducing peel adhesion.

EXAMPLES 28-31

A 96:4 isooctyl acrylate:acrylamide copolymer, having an inherent viscosity of 0.85, was dissolved in a 40:60 ethyl acetate:heptane blend to form a 24% solids solution. To 100 pbw aliquots of this solution were added various amounts of "Expancel" DE hollow polymeric microspheres. The resultant compositions were

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coated on an silicone liner, dried, and tested as in Examples 25-27, with the following results:

TABLE VII

| Example | Parts "Expancel" DE/100 parts adhesive solids | Percent "Expancel" by volume | Dried Thick- ness, micro- meters | Adhesion, N/cm | |
|-----------------|--|------------------------------------|--|----------------|-----------------|
| | | | | Liner side | Exposed side |
| 28 (Control) | 0 | 0 | 58 | 6.2 | 3.7 |
| 29 | 2.1 | 46 | 92 | 4.6 | 2.9 |
| 30 | 4.2 | 58 | 124 | 4.0 | 1.0 |
| 31 | 6.3 | 68 | 173 | 2.3 | 0.8 |

EXAMPLES 32 and 33

6 parts of a solid 94:6 isooctyl acrylate:acrylic acid copolymer was dissolved in 91 parts of isooctyl acrylate monomer and 9 parts acrylic acid then added. To 100 parts of this syrup was added 0.17 part HDDA, 0.20 part "Irgacure" 651, 6.0 parts hydrophobic silica ("Aerosil" R-972), and 0.5 part polyacrylonitrile fibers having a diameter of 30 micrometers and a length of 4.0 mm (Drhm 6.7/4, available from Bayer). The adhesive dispersion was then divided into equal portions. To one portion was added 16.0% glass microspheres (control Example 32), and to the other portion was added a mixture of 8.0% glass microspheres and 2.0% "Expancel" 551DE expanded polymeric microspheres (Example 33). Each portion was thoroughly mixed with a propeller stirrer, degassed in a desiccator, and polymerized between two silicone-coated polyester film liners, using 440 mJ/cm² of fluorescent black light to effect curing. The thickness of each adhesive layer was 800 micrometers. The dried adhesive of control Example 32 contained 13.1% glass microspheres by weight, equivalent to 48.4% by volume. The dried adhesive of Example 33 contained, on a weight basis, 6.9% glass microspheres and 1.7% polymeric microspheres, corresponding respectively to 24.6% and 23.1% by volume. A number of tests were then performed to determine the physical characteristics of the two adhesives. Results are tabulated below:

TABLE VIII

| Test | Example | |
|-------------------------------------|--------------|------|
| | 32 (control) | 33 |
| Tensile strength, N/mm ² | 0.42 | 0.57 |

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TABLE VIII-continued

| Test | Example | |
|--|--------------|---------|
| | 32 (control) | 33 |
| 5 Elongation at break, % | 167 | 246 |
| T-peel, N/cm width | 16.5 | 19.3 |
| Static shear, room temperature, 1250 g weight, stainless steel substrate, minutes | 120 | 10,000+ |
| 10 Static shear, room temperature, 1500 g weight, stainless steel substrate, minutes | 100 | 10,000+ |
| Static shear, 40° C., 1250 g weight, stainless steel substrate, minutes | 1700 | 10,000+ |
| 15 Static shear, 70° C., 1250 g weight, stainless steel substrate, minutes | 14 | 6000 |
| 20 Static shear, room temperature, 1000 g weight, cellulose nitrate substrate, minutes | 500 | 10,000+ |

The foregoing data show that the tensile strength of the adhesive containing both glass microbubbles and hollow polymeric microspheres (Example 33) was approximately 25% greater than that of a comparable adhesive containing only glass microbubbles (control Example 32), and the T-peel tensile strength was approximately 15% greater. Shear adhesion of the product of Example 33, was far superior to that of control Example 32. The product of Example 33 was found to be useful for mounting mirrors on nitrocellulose lacquer surfaces.

EXAMPLES 34-38

An 89:6:5 isooctylacrylate:acrylic acid: (methacrylate-capped 10,000 MW polystyrene*) terpolymer PSA was prepared in 70:30 toluene:ethyl acetate solvent. The resultant 47% solids solution, having a viscosity of 8.6 Pa.s, was then divided into five equal portions. The control (control Example 34) was used as prepared, while to Examples 35, 36, 37, and 38 were added, respectively, 1.06%, 2.13%, 3.19% and 4.26% by weight of "Expancel" DE 551 hollow microspheres. Each of the compositions was coated on a silicone liner, dried for 5 minutes at room temperature and 10 minutes at 70° C. and then evaluated. Results are tabulated below:

*Commonly referred to as a "macromer", available from Arco.

TABLE IX

| | | Example | | | | |
|--|------------|---------|-------|-------|--------|--------|
| | | Control | 34 | 35 | 36 | 37 |
| "Expancel" (weight %) | | 0.00 | 1.06 | 2.13 | 3.19 | 4.26 |
| (volume %) | | 0.00 | 35.00 | 45.50 | 52.50 | 57.50 |
| Thickness, mm | | 0.21 | 0.24 | 0.35 | 0.29 | 0.307 |
| Coating weight, g/m ² | | 216 | 191 | 175 | 162 | 150 |
| Viscosity, Pa.s (Brookfield Spindle 7, 20 rpm) | | 4 | 16 | 24 | 35.6 | 51.6 |
| 180° Peel Adhesion, N/cm | | | | | | |
| Initial | Top side | 6.26 | 4.99 | 3.97* | 3.63* | 3.80* |
| | Liner side | 6.64 | 6.37 | 2.17 | 3.14 | 3.04 |
| 24 Hrs RT | Top side | 10.40 | 10.23 | 8.37 | 7.46 | 3.04 |
| | Liner side | 8.32 | 7.93 | 4.72 | 5.87 | 6.99 |
| 48 Hrs RT | Top side | 12.65 | 12.85 | 10.31 | 13.63* | 13.02* |
| | Liner side | 9.63 | 8.96 | 5.25 | 7.23 | 7.28 |

TABLE IX-continued

| | Example | | | | |
|-------------------------------------|---------------|------|------|------|------|
| | Control 34 | 35 | 36 | 37 | 38 |
| Liner release, cN/cm | 6.38 | 4.13 | 3.31 | 2.28 | 2.68 |
| Static Shear, 250 g weight, minutes | | | | | |
| Room Temperature | 1210 | 1444 | 1312 | 502 | 765 |
| 70° C. | 34 | 26 | 12 | 18 | 17 |

*Adhesive split

EXAMPLES 39 AND 40

A 28% solids solution of 91:9 isooctyl acrylate:N-vinylpyrrolidone copolymer, having an inherent viscosity of 1.49 was prepared in 40:60 ethyl acetate:heptane and divided into two equal portions. One portion (control Example 39) was used as prepared. To the other portion (Example 40) was added 2.5% by weight "Expancel" DE hollow microspheres. Each of the two compositions was then coated on a silicone liner, dried, and evaluated. Results are tabulated below:

TABLE X

| Example | Parts "Expancel" DE/100 | Percent "Expancel" by volume | Dried thickness, micro- meters | Adhesion, N/cm | |
|-----------------|-------------------------------|------------------------------------|---|----------------|-----------------|
| | parts adhesive | | | Liner side | Exposed side |
| 39 (Control) | 0 | 0 | 90 | 6.4 | 4.4 |
| 40 | 2.5 | 48 | 136 | 4.8 | 2.4 |

EXAMPLES 41 AND 42

An 87.5:12.5 isooctylacrylate:acrylic acid monomer blend was partially thermally polymerized (8% conversion) to yield a syrup. To each of two 100 g aliquots of this syrup was added 0.055 g 1,6-hexanediol diacrylate (HDDA) crosslinking agent, 0.19 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) initiator, and 2.0 g hydrophilic silica ("Aerosil" 200). To the Example 41 aliquot was added 8.0 grams 3M "Scotchlite" C15/250 glass bubbles, and to the Example 42 aliquot was added 2.15 g "Expancel" 551DE polymeric microspheres, the density of the resultant adhesive in each case being approximately 0.75 g/cc. Each aliquot was thoroughly mixed using a propeller stirrer, degassed in a desiccator, and polymerized between two silicone-coated polyester film release liners, using 410 mJ/cm² of fluorescent black light to effect curing. In each case the thickness of the cured adhesive layer was 800 micrometers. The two adhesive layers displayed the following physical characteristics:

TABLE XI

| Physical Characteristic | Example | |
|-------------------------------------|---------------|------|
| | Control 41 | 42 |
| Tensile strength, N/mm ² | 1.09 | 1.69 |
| Elongation at break, % | 775 | 820 |
| T-peel, N/cm | 30.5 | 35.5 |

Over each side of one portion of each adhesive layer (hereinafter designated "A") was then laminated a 50-micrometer thick solvent-polymerized 90:10 isooctylacrylate:acrylic acid PSA, crosslinked with a bisaziri-

dine. In the same manner, to each side of another portion of each adhesive layer (hereinafter designated "B") was laminated a 50-micrometer thick solvent-polymerized 57.5:35.0:7.5 isooctylacrylate:methylacrylate:acrylic acid PSA, crosslinked with a bisaziridine.

Each of the four adhesive products was then adhered to a steel panel painted with automotive enamel (Ford 50J107A), and the force required to initiate and continue removal was measured after various lengths of time at different environmental conditions with the results shown below:

TABLE XII

| Force required to initiate removal, N/cm, after dwell time indicated | | | | | |
|---|--------------------------------------|----------------|-----|----------------|-----|
| Dwell time | Environmental conditions of dwell | Example | | | |
| | | Control 41A | 42A | Control 41B | 42B |
| 2 minutes | Room temperature | 81 | 93 | 113 | 121 |
| 72 hours | Room temperature | 145 | 150 | 146 | 159 |
| 72 hours | 38° C., 100% RH | 113 | 124 | 125 | 143 |

TABLE XIII

| Force to continue peel, N/cm width | | | | | |
|------------------------------------|--------------------------------------|----------------|-----|----------------|-----|
| Dwell time | Environmental conditions of dwell | Example | | | |
| | | Control 41A | 42A | Control 41B | 42B |
| 2 minutes | Room temperature | 39 | 42 | 46 | 54 |
| 72 hours | Room temperature | 71 | 71 | 69 | 94 |
| 72 hours | 38° C., 100% RH | 55 | 70 | 59 | 71 |

In all tests conducted after 2 minutes dwell time, the adhesive popped off the painted panel; in all other tests, the adhesive layer split during removal.

EXAMPLES 43 AND 44

A 91:9 isooctylacrylate:acrylic acid monomer blend was partially thermally polymerized (11% conversion) to yield a syrup. To each of two 100 g aliquots of this syrup was added 0.05 g 1,6-hexanediol diacrylate (HDDA), 0.15 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) initiator, and 4 g fumed silica. To the first aliquot (Example 43) was added 2 g glass microspheres and 1.5 g "Expancel" DE 551 expanded polymeric microspheres; to the second aliquot (Example 44) was added 6 g glass microspheres and 0.5 g "Expancel" 551 microspheres. Each sample was thoroughly mixed, using a propeller stirrer, degassed in a desiccator, and polymerized between two silicone-coated polyester film liners using 2,369 mJ/cm² of fluorescent black light to effect curing. In each case the resultant product was a 3,500-micrometer layer of a crosslinked acrylate PSA

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containing 45% microspheres by volume and useful for glazing, e.g., mounting windshields in automobiles.

EXAMPLES 45-48

A 91:9 isooctylacrylate:acrylic acid blend was partially thermally polymerized (14% conversion) to yield a syrup. To each of four 100 g aliquots of this syrup was added 0.05 g 1,6-hexanediol diacrylate (HDDA), 0.15 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) initiator, 4 g fumed silica ("Aerosil" R-972), and 2.15 g expanded polymeric microspheres ("Expancel" DE 551). To the four aliquots were then added varying weights of unexpanded polymeric microspheres ("Expancel" DU). Each aliquot was thoroughly mixed using a propeller stirrer, degassed in a desiccator, and polymerized between two silicone-coated polyester film liners using 386 mJ/cm² of fluorescent black light to effect curing. A number of tests were then performed on each of the adhesive layers, with the results shown below:

TABLE XIV

| Test | Example | | | |
|---|---------|---------|---------|---------|
| | 45 | 46 | 47 | 48 |
| Weight % "Expancel" DU added | 0 | 1 | 2 | 3 |
| Thickness, micrometers | 900 | 900 | 900 | 890 |
| Tensile strength, N/mm ² | 1.15 | 1.26 | 1.25 | 1.20 |
| Elongation at break, % | 656 | 727 | 732 | 718 |
| Static shear, 1 kg weight, 70° C., min. | 10,000+ | 10,000+ | 10,000+ | 10,000+ |

Samples of each adhesive layer were laminated to (1) steel panels painted with automotive enamel and (2) stainless steel panels and allowed to dwell for 72 hours at room temperature. The 180° peel adhesion test was then used to measure the force required to initiate removal of the adhesive strip, as well as the force required to continue removal. Identical panels, each bearing its respective adhesive layer, were allowed to dwell for 72

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TABLE XV-continued

| Test | Example | | | |
|--|---------|------|------|------|
| | 45 | 46 | 47 | 48 |
| Peel adhesion to automotive enamel, N/cm width | | | | |
| To initiate removal | | | | |
| Before heating | 104 | 104 | 112 | 98 |
| After heating | 54 | 65 | 85 | 65 |
| To continue removal | | | | |
| Before heating | 19.8 | 20.0 | 23.0 | 21.0 |
| After heating | 14.5 | 20.3 | 15.6 | 9.8 |
| Peel adhesion to stainless steel, N/cm width | | | | |
| Before heating | 12.6 | 13.4 | 13.0 | 12.2 |
| After heating | 32.3 | 29.9 | 31.1 | 31.1 |

It is interesting to note that expansion of the microspheres appears to decrease the adhesion to automotive enamel but increase the adhesion to stainless steel.

EXAMPLES 49-55

An 87.5:12.5 isooctyl acrylate:acrylic acid monomer blend containing 0.04 part per hundred 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) was photopolymerized (8% conversion) to yield a syrup. To each of ten 250 g aliquots of this syrup was added to 0.25 g "Irgacure" 651, 0.125 g 1,6-hexanediol diacrylate (HDDA) crosslinker, 10.0 g "Aerosil" R-972 fumed silica and the amount of polymeric microspheres specified in table XVI. Each aliquot was thoroughly mixed with a propeller stirrer, degassed in a desiccator, repurged with nitrogen, and polymerized between two silicone-coated polyester release liners, using 450 mJ/cm² of fluorescent black light to achieve cure. The samples were 1.0-1.09 mm thick. Tensile properties as reported in Table XVI were then obtained.

Acrylate-based PSAs were laminated to both sides of this core, and peel adhesion tests conducted using a low solids lacquer paint substrate. Results are also included in Table XVI.

TABLE XVI

| Ex. | Expancel 551 DE (wt. %) | "Expancel" 551 DE (Percent by Vol.) | Density (g/cm ³) | Peak Tensile Stress (N/mm ²) | Elongation at Break (Percent) | Energy to Break (cm-N) | T-Peel (N/cm) | 90° Peel Adhesion (N/cm) | 180° Peel Adhesion (N/cm) |
|-----|-------------------------|-------------------------------------|------------------------------|--|-------------------------------|------------------------|---------------|--------------------------|---------------------------|
| 49 | 0 | 0 | 1.03 | 1.05 | 901 | 127 | 45.3 | 48.8 | 35.7 |
| 50 | 0.93 | 20 | 0.88 | 1.28 | 860 | 191 | 54.9 | 54.7 | 37.2 |
| 51 | 1.59 | 30 | 0.78 | 1.42 | 876 | 240 | 44.4 | 59.8 | 39.4 |
| 52 | 2.44 | 40 | 0.69 | 1.37 | 776 | 233 | 41.6 | 85.8 | 42.3 |
| 53 | 3.62 | 50 | 0.58 | 1.23 | 606 | 180 | 39.2 | 77.1 | 42.9 |
| 54 | 5.34 | 60 | 0.48 | 1.03 | 321 | 85.4 | 30.2 | 59.3 | 43.1 |
| 55 | 8.07 | 70 | 0.35 | 0.64 | 169 | 32.5 | 10.5 | 19.9 | 16.9 |

hours at room temperature and then placed in a 120° C. oven for five minutes to expand the "Expancel" DU microspheres, after which the same tests were conducted. Results are tabulated below:

TABLE XV

| Test | Example | | | |
|---------------------------------|---------|-----|-----|------|
| | 45 | 46 | 47 | 48 |
| Adhesive thickness, micrometers | 900 | 940 | 970 | 1000 |
| Total volume % microspheres | 40 | 50 | 53 | 57 |

EXAMPLES 56, 57

A 91:9 (Example 56) and a 93:7 (Example 57) isooctylacrylate:acrylic acid blend were partially thermally polymerized (8% conversion) to yield syrups. To 100 g of each syrup 0.11 g 1,6-hexanediol diacrylate (HDDA) crosslinker and 0.20 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) photoinitiator was added.

To the syrup of Example 56 was then added 2.15 g (32.3% by volume) expanded polymeric microspheres ("Expancel" 551 DE) and 4.00 g hydrophobic fumed

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silica ("Aerosil" R-972), to the syrup of Example 57 2.50 g (35.6% by volume) polymeric microspheres and 6.00 g hydrophobic fumed silica were added.

The filled syrup of each example was thoroughly mixed using a propeller stirrer, degassed in a desiccator and polymerized between two silicone coated polyester film liners using 410 mJ/cm² of fluorescent black light to effect curing. In the first 3% of the curing chamber for Example 56 relatively low intensity light and for Example 57 relatively high intensity light was used.

In each case the thickness of the cured crosslinked acrylate PSA layer was 800 micrometers. A number of tests were then performed on each of the adhesives with results as shown below:

TABLE XVII

| | Example | |
|---|---------|---------|
| | 56 | 57 |
| Foam density, kg/m ³ | 730 | 710 |
| Tensile strength, N/mm ² | 1.37 | 1.06 |
| Secant modulus, N/mm ² | | |
| 20% | 0.80 | 0.70 |
| 100% | 0.32 | 0.26 |
| Elongation at break, % | 771 | 914 |
| T-peel tensile strength, N/cm | 32.0 | 31.0 |
| High temperature static shear (70° C., 1000 g wt), minutes to failure | 10,000+ | 10,000+ |

TABLE XVIII

| 90° Peel Adhesion to Stainless Steel, n/cm width | | | |
|--|-----------------------------------|----------|------|
| Dwell Time | Environmental conditions of dwell | Examples | |
| | | 56 | 57 |
| 2 minutes | room temperature | 12.9 | 11.1 |
| 20 minutes | room temperature | 17.1 | 14.2 |
| 3 days | room temperature | 25.6 | 27.5 |

When the tapes of Examples 56 and 57 were adhered to a steel panel painted with automotive paint (Opel, VW) the force required to initiate and continue removal of an attached vinyl bar was measured, with results as shown below:

TABLE XIX

| Dwell time | Environmental conditions of dwell | Paint | Force to initiate removal, N/cm | | Force to continue peel, N/cm | |
|------------|-----------------------------------|-------|---------------------------------|--------|------------------------------|--------|
| | | | Ex. 56 | Ex. 57 | Ex. 56 | Ex. 57 |
| 72 hrs. | room temp. | Opel | 111.3 | 95.2 | 27.9 | 20.4 |
| 72 hrs. | room temp. | VW | 112.6 | 85.4 | 29.6 | 19.4 |

EXAMPLES 58-63

A 91:9 and an 87.5:12.5 isooctyl acrylate:acrylic acid blend were both partially polymerized (8% conversion) to yield syrups. To each of three 100 g samples of each syrup were added 0.20 g 1,6-hexanediol diacrylate (HDDA) crosslinker, 0.20 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) photoinitiator and 6.00 g hydrophobic fumed silica ("Aerosil" R-972). Polymeric microspheres ("Expancel" 551 DE) were then added. Each sample was thoroughly mixed using a propeller stirrer, degassed in a desiccator and polymerized between two silicone-coated polyester film liners,

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using 509 mJ/cm² of fluorescent black light to effect curing.

In each case the thickness of the cured crosslinked acrylate PSA layer was 800 micrometers.

A number of tests were then performed on each of the adhesives with results as shown below:

TABLE XX

| Example | 58 | 59 | 60 | 61 | 62 | 63 |
|-------------------------------------|------|------|-------|-------|-------|-------|
| Isooctylacrylate | 91:9 | 91:9 | 91:9 | 87.5: | 87.5: | 87.5: |
| Acrylic Acid | | | | 12.5 | 12.5 | 12.5 |
| Ratio | | | | | | |
| "Expancel" 551 DE | | | | | | |
| weight, g | 2.15 | 3.50 | 5.00 | 2.15 | 3.50 | 5.00 |
| Volume % | 32.1 | 43.5 | 52.3 | 32.1 | 43.5 | 52.3 |
| Foam Density, kg/m ³ | 760 | 640 | 530 | 750 | 640 | 550 |
| Tensile Strength, N/mm ² | 1.41 | 1.13 | 1.05 | 1.71 | 1.54 | 1.34 |
| Secant Modulus, N/mm ² | | | | | | |
| 20% | 0.85 | 1.20 | 1.70 | 1.40 | 1.70 | 2.30 |
| 100% | 0.35 | 0.49 | 0.59 | 0.58 | 0.70 | 0.84 |
| Elongation at break, % | 695 | 407 | 375 | 585 | 536 | 381 |
| T-peel tensile, N/cm | 31.0 | 30.3 | 25.8 | 41.8 | 35.3 | 27.8 |
| 90° Peel Adhesion, N/cm | | | | | | |
| Substrate Dwell Time | | | | | | |
| Stainless Steel | | | | | | |
| 2 minutes | 12.3 | 12.2 | 11.6 | 11.0 | 12.7 | 10.6 |
| 20 minutes | 16.8 | 16.3 | 14.6 | 19.8 | 21.5 | 20.2 |
| 3 days | 29.9 | 26.9 | 32.1* | 53.2 | 54.6 | 41.7* |
| Polypropylene | | | | | | |
| 2 minutes | 2.1 | 1.7 | 1.9 | 0.8 | 0.9 | 0.9 |
| 20 minutes | 4.7 | 3.2 | 2.7 | 1.4 | 1.6 | 1.0 |
| 3 days | 4.2 | 2.3 | 3.3 | 1.5 | 1.2 | 1.1 |

*Foam split (all others popped off panel)

EXAMPLES 64, 65

A 91:9 isooctylacrylate:acrylic acid blend was partially thermally polymerized (6.5% conversion) to yield a syrup. To two 100 g samples of this syrup 0.18 g 1,6-hexanediol diacrylate (HDDA) crosslinker, 0.20 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) photoinitiator, 6.00 g hydrophobic fumed silica "Aerosil" R-972 and 0.5 g polyacrylonitrile fibers having a diameter of 30 micrometers and a length of 4.0 mm (Dralon Drhm 6.7/4, available from Bayer) were added. To the blend of Example 64, 8.00 g glass microspheres and 1.75 g "Expancel" 551 DE expanded polymeric microspheres were added; to the blend of Example 65, only 3.75 g "Expancel" 551 DE was added. Each sample was thoroughly mixed using a propeller stirrer, degassed in a desiccator and polymerized between two silicon coated polyester film liners using 300 mJ/cm² of fluorescent black light to effect curing. In each case the thickness of the cured crosslinked acrylate PSA layer was 800 micrometers.

TABLE XXI

| | Example | |
|------------------------------------|---------|------|
| | 64 | 65 |
| Vol. % glass microspheres | 25.3 | |
| Vol. % polymeric microspheres | 20.8 | 45.2 |
| Total Vol. % microspheres | 46.1 | 45.2 |
| Foam density, kg/m ³ | 590 | 620 |
| T-peel tensile strength N/cm width | 24.9 | 27.5 |

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TABLE XXI-continued

| | Example | |
|--|---------|------|
| | 64 | 65 |
| Tensile strength, N/mm ² | 0.81 | 0.59 |
| Secant modulus, 20%, N/mm ² | 0.61 | 0.59 |
| Elongation % | 108 | 233 |
| 90° peel adhesion to stainless steel, N/cm | | |
| 2 minutes dwell | 14.0 | 11.8 |
| 20 minutes dwell | 26.0 | 19.0 |

EXAMPLES 66-68

A 91:9 isooctylacrylate:acrylic acid monomer blend was partially U.V. polymerized (8% conversion) to yield a syrup. To each of three 100 g aliquots of this syrup was added 0.08 g 1,6-hexanediol diacrylate (HDDA) crosslinking agent, 0.14 g 2,2-dimethoxy-2-phenyl acetophenone ("Irgacure" 651) initiator, and 6.0 g hydrophobic silica ("Aerosil" 972). To each Example was added 2.15 g "Expancel" 551DE polymeric microspheres, the density of the resultant adhesive in each case being approximately 0.75 g/cc. Each aliquot was thoroughly mixed using a propeller stirrer and degassed in a desiccator. Two of the three microbubble-filled mixture (Examples 70 and 71) were frothed as taught in "Typical Tape-Making Procedure" of U.S. Pat. No. 4,415,616.

TABLE XXII

| | Example | | |
|-------------------------------------|---------|------|------|
| | 66 | 67 | 68 |
| Tensile Strength, N/mm ² | 1.42 | 0.82 | 0.74 |
| Elongation at break, % | 860 | 884 | 762 |
| T-peel, N/cm | 36.5 | 12.7 | 11.6 |
| Density, g/cm ³ | 0.74 | 0.69 | 0.64 |

Each of the three adhesive products were adhered to a steel panel painted with automotive enamel (Ford 50J107A), and the force required to initiate and continue removal was measured after various lengths of time at different environmental conditions, with the results shown below:

TABLE XXIII

| Dwell time | Environmental Conditions of Dwell | Force Required to Initiate Removal, N/cm Example | | | Force Required to Continue Removal, N/cm | | |
|------------|-----------------------------------|--|----|----|--|----|----|
| | | 66 | 67 | 68 | 66 | 67 | 68 |
| 2 min. | Room temp. | 57 | 40 | 43 | 14 | 12 | 12 |
| 72 hrs. | Room temp. | 103 | 88 | 84 | 31 | 24 | 25 |
| 72 hrs. | 38° C., 100% RH | 128 | 87 | 89 | 46 | 39 | 39 |

In all tests conducted after 2 minutes dwell time, the adhesive popped off the painted panel; in all other tests, the adhesive layer split during removal.

We claim:

1. Pressure-sensitive adhesive-coated sheet material comprising in combination a sheet backing bearing on at least one surface a layer of normally tacky and pressure-sensitive adhesive on the order of at least 20 micrometers thick, said layer containing from about 1/5 to about 2/3% by volume of resilient non-tacky hollow thermoplastic polymeric spheres having a diameter in the ap-

proximate range of 10-125 micrometers, substantially all of said spheres having an actual density on the order of 0.01-0.04 g/cc and a shell thickness on the order of 0.02 micrometers and being substantially completely surrounded by the pressure-sensitive adhesive.

2. The sheet material of claim 1 wherein at least about 2/3 of said spheres have a diameter in the range of 30-70 micrometers.

3. The sheet material of claim 2 wherein the layer of normally tacky and pressure sensitive is on the order of 20-4000 micrometers thick.

4. The sheet material of claim 2 wherein the hollow polymeric spheres are formed of vinylidene chloride-acrylonitrile copolymer, the adhesive layer containing about 1/5 to about 1/2 polymeric spheres on a volume basis and being capable of substantially complete recovery after being subjected to a temporary compressive pressure of 15 kPa, said adhesive maintaining good adhesion to substrate even when subjected to mechanical shock at extremely low temperatures.

5. The sheet material of claim 1 wherein the hollow polymeric spheres are formed of vinylidene chloride-acrylonitrile copolymer.

6. The sheet material of claim 5 wherein the adhesive layer is permanently bonded to the backing.

7. The sheet material of claim 6 wherein the thickness of the adhesive layer is on the order of 40-80 micrometers and contains at least 50% of the hollow polymeric spheres on a volume basis, said adhesive layer being capable of substantially complete recovery after being subjected to a temporary compressive pressure of 15 kPa, and the exposed surface of the adhesive layer having an irregular contour caused by the presence of the hollow polymeric spheres, whereby said sheet material can be repeatedly adhered to paper substrates and removed without tearing the paper, a sheet of material identical except that the exposed surface of the adhesive is substantially planar, not being removable from paper substrates, after being applied thereto, without tearing the paper.

8. The sheet material of claim 5 wherein the adhesive layer is strippably bonded to the backing.

9. The sheet material of claim 8 wherein the exposed surface of the adhesive layer has an irregular contour caused by the presence of the hollow polymeric spheres, the surface of the adhesive layer in contact with the sheet backing being smooth and uniform, whereby said sheet material can be removed from the backing to provide a transfer tape having lower adhesive properties at the initially exposed surface than at the surface initially in contact with the backing.

10. The sheet material of claim 8 wherein the adhesive layer is on the order of one millimeter thick and one surface thereof is strippably bonded to a smooth-surfaced backing, yielding a foam tape especially suited for mounting applications that will be exposed to low temperatures.

11. The sheet material of claim 8 wherein the adhesive layer is on the order of 3-4 millimeters thick and is especially adapted to glazing.

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12. The sheet material of claim 8 wherein glass microspheres are also present in the adhesive layer.

13. The sheet material of claim 8 wherein gas-filled voids are also present in the adhesive layer.

14. The sheet material of claim 5 wherein the pressure-sensitive adhesive is a copolymer of isooctyl acrylate and at least one other monoethylenically unsaturated monomer.

15. The sheet material of claim 14 wherein the other monomer is acrylic acid.

16. The sheet material of claim 14 wherein the adhesive contains UV initiator.

17. The sheet material of claim 14 wherein the other monomer is acrylamide.

18. The sheet material of claim 14 wherein one of the other monomers is N-vinyl pyrrolidone.

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19. The sheet material of claim 14 wherein a tackifier is also included.

20. The sheet material of claim 14 wherein the adhesive is an isooctylacrylate:acrylic acid:macromer terpolymer, the macromer being methacrylate-capped polystyrene.

21. The sheet material of claim 5 wherein the pressure-sensitive adhesive is a rubber-resin composition.

22. The sheet material of claim 21 wherein the adhesive layer contains at least about $\frac{1}{4}$ hollow spheres by volume.

23. The sheet material of claim 5 wherein a layer of essentially void-free normally tacky and pressure-sensitive adhesive is laminated to at least one face of the microsphere-filled adhesive layer.

24. The sheet material of claim 5 wherein a layer of normally tacky and pressure-sensitive adhesive is adhered to the opposite surface of the backing.

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US005153041A

United States Patent [19][11] **Patent Number:** **5,153,041****Clements et al.**[45] **Date of Patent:** **Oct. 6, 1992**[54] **PAD ASSEMBLY**

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[21] **Appl. No.:** **595,319**

[22] **Filed:** **Oct. 10, 1990**

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[52] **U.S. Cl.:** 428/40; 428/77; 428/138; 428/194; 428/202; 281/15.1; 283/63.1; 462/55

[58] **Field of Search:** 428/40, 77, 194, 202, 428/138; 281/15.1; 283/63.1; 462/55

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Primary Examiner—Alexander S. Thomas

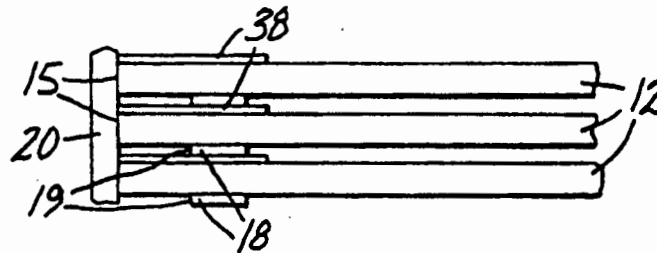
Attorney, Agent, or Firm—Gary L. Griswold; Walter N. Kirn; William L. Huebsch

[57] **ABSTRACT**

A pad assembly comprising a multiplicity of flexible

sheets each having a band of repositionable pressure sensitive adhesive coated on its rear surface adjacent and spaced by a small predetermined spacing from a first edge. The sheets are disposed in a stack with the band of repositionable pressure sensitive adhesive on each sheet adhering it to the adjacent sheet in the stack; and a layer of padding compound is disposed over and adhered to aligned first edges of the sheets in the stack. The padding compound allows, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet (and any sheets above it) to be pivoted away from that adjacent sheet while remaining adhered to the adjacent sheets. The small predetermined spacing between the band of repositionable pressure sensitive adhesive and the first edge of each sheet provides a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack separates from the front surface of the adjacent sheet in the stack that signals the person peeling the sheet away that such separation has occurred, and allows that person to reduce the force he is applying to the sheet, thereby restricting inadvertent separation of that sheet from the padding compound. After a sheet is intentionally separated from the padding compound, the band of repositionable pressure sensitive adhesive on the sheet affords adhesion of that sheet to a vertical surface.

12 Claims, 1 Drawing Sheet



U.S. Patent

Oct. 6, 1992

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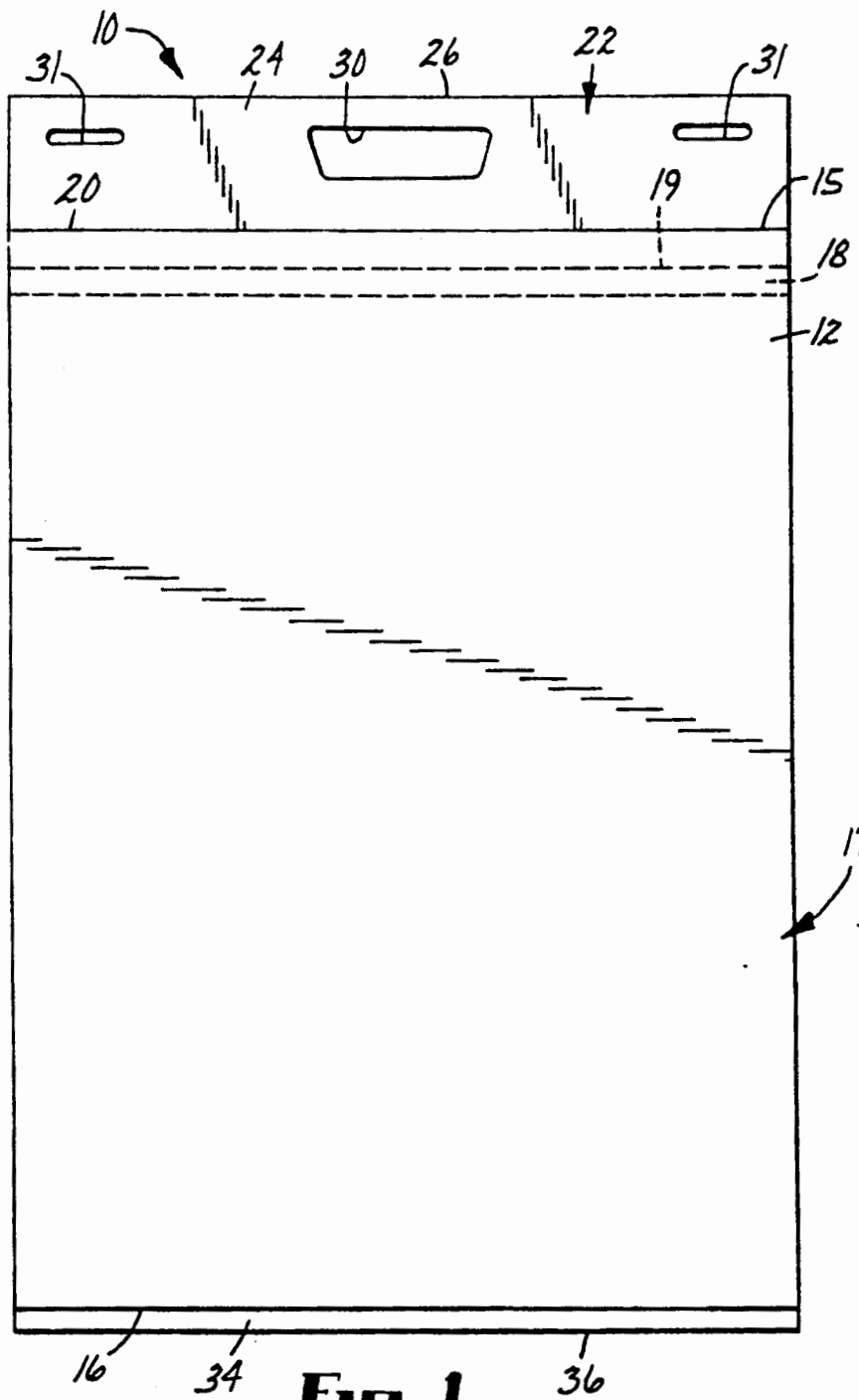


Fig. 1

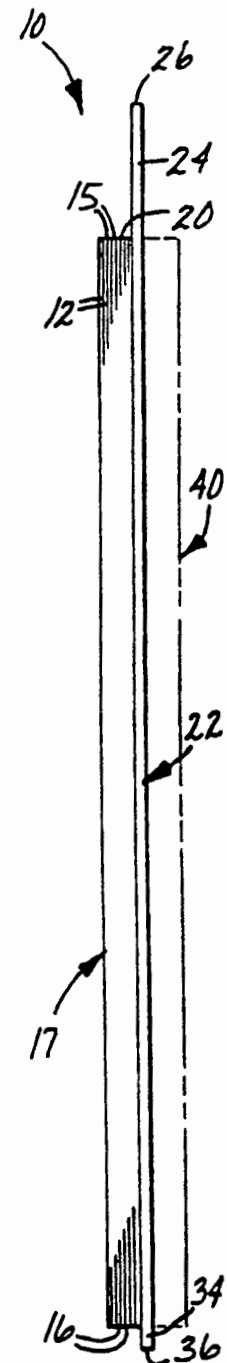


Fig. 2

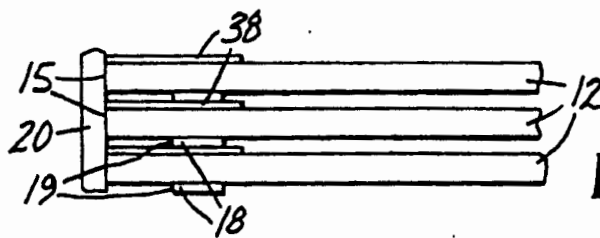


Fig. 3

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PAD ASSEMBLY

TECHNICAL FIELD

The present invention relates to pad assemblies of the type including a multiplicity of aligned flexible sheets in a stack which are attached together along or adjacent aligned edges of the sheets so that any of several uppermost individual sheets in the stack can either (1) be bent or pivoted away from an adjacent underlying sheet so that the underlying sheet can be written on, or (2) be separated from the stack so that the separated sheets can be used elsewhere or disposed of; and in one important aspect, to such pad assemblies that are large in size, and in which the stack is mounted on a stiff back card so that the pad assembly can be supported in a vertical position at the front of a room during a meeting and used to record lists of items or ideas generated during the meeting.

BACKGROUND ART

Many pad assemblies include a multiplicity of aligned flexible sheets (i.e., typically paper sheets) in a stack which are attached together along or adjacent aligned edges of the sheets. Some such pad assemblies are large in size and include a stiff back card on which the stack is mounted so that the pad assembly can be supported at the front of a room on a support such as an easel during a meeting and used to record lists of items or ideas generated during the meeting. During such use, typically one or more of the uppermost sheets on the pad, after being written on, are either (1) bent or pivoted away from an underlying sheet so that they project over and are supported on an upper support edge of the back card and the underlying sheet can be written on, or (2) are separated from the stack so that the separated sheet or sheets can be positioned elsewhere, typically on the walls of the room to which they are attached by means such as a clip, pin or a length of adhesive coated tape so that information on the separated sheets can easily be viewed by the participants of the meeting. In some such pad assemblies the sheets are attached together by a layer of padding compound along the one edge portion which allows the individual sheets to be separated from the padding compound or pivoted away from underlying sheets by bending the layer of padding compound. In the most common type of such pad assemblies the sheets are attached together by staples through portions of the sheets adjacent the aligned edges of the sheets. Such staples more firmly hold the sheets together, but require portions of the sheets around the staples to be bent when the sheets are supported on the support edge and to be torn away when the sheets are removed from the pad; whereas in yet other type of such pad assemblies the sheets are attached together by staples through portions of the sheets adjacent the aligned edges of the sheets and are transversely perforated just below the staples so that the sheets can be torn off along their lines of perforation, or folded along the lines of perforations when the sheets are supported on the support edge.

A pad assembly commercially designated "Clingers" and available from the Ampad Corporation, Holyoke, Md., comprises a multiplicity of flexible sheets disposed in a stack with the corresponding edges of the sheets aligned and with each sheet having a band of repositionable pressure sensitive adhesive coated on its rear surface along aligned first edges of the sheets, and the band of repositionable pressure sensitive adhesive on each

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sheet adhering it to the front surface of the adjacent sheet in the stack. Sheets removed from the "Clingers" pad assembly can be releasably adhered to a support surface by the bands of repositionable pressure sensitive adhesive on the sheets. Only the top sheet from such a pad assembly can be easily removed, however, which is a significant disadvantage of such a pad assembly compared to the pad assemblies described above from which underlying sheets in the pad can be easily removed prior to removal of the uppermost sheet in the pad. Also, the pressure sensitive adhesive on the sheets from the "Clingers" pad assembly will not stick very long to anything but the smoothest of wall surfaces, such as painted sheet rock and metal surfaces, glass, or the like.

DISCLOSURE OF INVENTION

The present invention provides a pad assembly of the type including a multiplicity of aligned flexible sheets attached together along one edge portion to form a stack from which any of several uppermost individual sheets can either be pivoted away from an adjacent sheet, or can be separated from the stack and releasably adhered to a support surface by repositionable pressure sensitive on the sheet that can adhere well to many rough surfaces; which pad assemblies are particularly useful when made large in size and to include a stiff back card whereby they can be supported at the front of a room during a meeting in a generally vertical position and used to record lists of items or ideas generated during the meeting.

According to the present invention there is provided a pad assembly comprising a multiplicity of flexible sheets each having a band of repositionable pressure sensitive adhesive coated on its rear surface adjacent to and spaced by a small predetermined spacing from a first edge and spaced by a large predetermined spacing from a second opposite edge. The sheets are disposed in a stack with the corresponding edges of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering it to the adjacent sheet in the stack. A layer of padding compound is disposed over and adhered to the aligned first edges of the sheets in the stack. The padding compound is sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet (and any sheets above it) to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets. The padding compound will remain adhered to the adjacent sheets during such flexing while affording manual peeling of that one sheet from the padding compound to separate that one sheet from the stack. The small predetermined spacing between the band of repositionable pressure sensitive adhesive and the first edge of each sheet provides a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack has been separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets, which tactile feel allows the user to reduce the peeling force being manually applied to the sheet and thereby restricts inadvertent separation of that sheet from the padding compound; and after that sheet is intentionally separated from the padding compound,

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the band of repositionable pressure sensitive adhesive on the sheet allows the user to removably adhere that sheet to a vertical support surface without the need to use tape, pins, or other separate attachment means.

The tactile feel that restricts inadvertent separation of that sheet from the padding compound is produced when that spacing is as little as 0.6 centimeter (0.25 inch) in a direction normal to the first edge of the sheet, and is well pronounced when that spacing is at least 1.2 centimeters (0.5 inch) or more. That spacing, however, preferably should not be greater than about 4 centimeters (1.5 inches) so that the portion of the sheet adjacent its first or top edge will be supported in a vertical position when a sheet is separated from the stack and adhered to a vertical surface by the band of repositionable pressure sensitive adhesive.

Preferably, when used as a flip chart, the pad assembly further includes a stiff back card to which the bottom most sheet in the stack is attached, which back card is at least coextensive with the sheets in the stack. That back card can have a top edge aligned with the first edges of the sheets, or, as illustrated herein, can have a top portion projecting past the aligned first edges of the sheets, which top portion has a peripheral support edge generally parallel to the first edges of the sheets over which support surface one or more of the sheets in the pad can be supported after they are peeled away from the adjacent underlying sheet. The top portion of the back card can have an elongate opening generally aligned with and spaced from that support edge with the part of the top portion between the opening and that support edge providing a handle by which the pad assembly can easily be moved from place to place. To provide space for that opening the top portion of the back card should project in the range of about 5 to 10 centimeters (2 to 4 inches) past the first edges of the sheets. Also, the top portion of the back card can have two aligned parallel elongate through slots positioned adjacent opposite sides of the back card and adapted to receive the support pegs on some types of easels on which the pad assembly might be supported.

BRIEF DESCRIPTION OF DRAWING

The present invention will be further described with reference to the accompanying drawing wherein like reference numerals refer to like parts in the several views, and wherein:

FIG. 1 is a front view of a pad assembly according to the present invention;

FIG. 2 is a side view of the pad assembly of FIG. 1; and

FIG. 3 is a fragmentary much enlarged side view of three sheets and the means by which they are attached together in the pad assembly of FIG. 1.

DETAILED DESCRIPTION

Referring now to the drawing, there is shown a pad assembly according to the present invention generally designated by the reference numeral 10, which pad assembly 10 is in an embodiment sometimes called a "flip chart" or an "easel pad" which can be supported on a support such as an easel (not shown) at the front of the room during a meeting and used to record lists of items or ideas generated during the meeting.

Generally the pad assembly 10 comprises (1) a multiplicity of flexible sheets 12 (e.g., 30 sheets 12), each sheet 12 being generally of the same size, having front and rear surfaces, having peripheral edges including

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first and second opposite edges 15 and 16, having a band 18 (see FIG. 3) of repositionable pressure sensitive adhesive coated on the rear surface adjacent to and spaced by a small predetermined spacing from the first edge 15 and spaced by a large predetermined spacing from the second edge 16, the sheets 12 being disposed in a stack 17 with the corresponding peripheral edges of the sheets 12 aligned, the front and rear surfaces of adjacent sheets 12 facing each other, and the band 18 of repositionable pressure sensitive adhesive on each sheet 12 adhering that sheet 12 to the adjacent sheet 12 in the stack 17; and (2) a layer 20 of padding compound disposed over and releasably adhered to the aligned first edges 15 of the sheets 12 in the stack 17. The layer 20 of padding compound is sufficiently flexible to allow, after the band 18 of repositionable pressure sensitive adhesive on the rear surface of one of the sheets 12 in the stack 17 is separated from the front surface of the adjacent sheet 12 in the stack 17, that one sheet 12 to be pivoted away from that adjacent sheet 12 by hinge-like flexing of the layer 20 of padding compound between the sheets 12, while the layer 20 of padding compound will remain adhered to the adjacent sheets 12 during such flexing while affording manual peeling of that one sheet 12 from the layer 20 of padding compound to separate that one sheet 12 from the stack 17.

The layer 20 of padding compound can be formed with any of several commercially available adhesive padding compound materials, such as "Merit" padding adhesive from Merrit Pad Co., Plainsville, Ohio; "Hurst Graphics" padding compound from Hurst Graphics, Los Angeles, Calif.; or "Champadco" padding cement from Champion Mfg. Co., Charlotte, N.C.

The sheets 12 can be of paper that weighs 18 pounds per ream 17 inch by 22 inch by 500 inch in size, such as the paper commercially designated "Form Run Bond" that is available from Georgia Pacific, Kalamazoo, Mich., and may, for example, have a dimension between the first and second edges 15 and 16 of about 775 millimeters (30.5 inches) and a width in a direction parallel to the first and second edge 15 and 16 of about 580 millimeters (22.8 inches).

The small predetermined spacing between the first edge 15 of each sheet 12 to which the layer 20 of padding compound is adhered and the adjacent edge 19 of the band 18 of repositionable pressure sensitive adhesive on each sheet 12 provides a tactile feel when the the band 18 of repositionable pressure sensitive adhesive on the rear surface of one of the sheets 12 in the stack 17 separates from the front surface of the adjacent sheet 12 in the stack 17 as the sheets are manually peeled apart. That tactile feel allows the person applying the peeling force to reduce or terminate it and thereby restricts inadvertent separation of that sheet 12 from the layer 20 of padding compound. For sheets 12 of the dimensions indicated above, the tactile feel that restricts inadvertent separation of one of the sheets 12 from the layer 20 of padding compound is most pronounced and effective when that spacing is at least 1.2 centimeters (0.5 inch) or more in a direction normal to the first edge 15 of the sheet 12, however the tactile feel is produced for sheets of that size when that spacing is as little as 0.6 centimeter (0.25 inch). After one of the sheets 12 is intentionally separated from the layer 20 of padding compound, the band 18 of repositionable pressure sensitive adhesive affords removably adhering that sheet 12 to a vertical support surface.

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The pad assembly 10 further includes a back card 22 of a stiff material (e.g., rigid cardboard or chipboard 864 millimeters (34 inches) high by 580 millimeters (22.8 inches) wide) having a front surface to which the rear surface of the bottom most sheet 12 in the stack 17 is attached. The front surface of the back card 22 is coextensive with the sheets 12 in the stack 17, and the back card 22 has a top portion 24 projecting past the aligned first edges 15 of the sheets 12. The top portion 24 has a peripheral support edge 26 generally parallel to the first edges 15 of the sheets 12 preferably spaced about 9 centimeters (3.5 inches) from the first edges 15 of the sheets 12, over which support edge 26 one or more of the sheets 12 in the stack 17 can be supported after the bands 18 of pressure sensitive on those sheets 12 have been peeled away from the adjacent underlying sheet 12 and those sheets 12 are bent back over the support edge 26. The top portion 24 has an elongate through opening 30 generally aligned with and spaced from the support edge 26 with the part of the top portion 24 between the opening 30 and the support edge 26 providing a handle for the pad assembly 10 by which the pad assembly 10 can conveniently be manually moved around. Also, the top portion 24 has two aligned, parallel elongate through slots 31 positioned adjacent opposite sides of the back card 22 and aligned parallel to the support edge 26, the slots 31 being adapted to receive the support pegs on some types of easels on which the pad assembly 10 might be supported.

The back card 22 also has a bottom portion 34 projecting past the aligned second edges 16 of the sheets 12. The bottom portion 34 has a peripheral supported edge 36 generally parallel to the second edges 16 of the sheets 12 and spaced in the range of about 0.6 to 2.5 centimeters (0.25 to 1 inch) and preferably about 1.3 centimeters (0.5 inch) from the second edges 16 of the sheets 12, which supported edge 36 is adapted to be supported on a support surface such as on the support ledge of an easel while the bottom portion 34 spaces the second edges 16 of the sheets 12 sufficiently from that support surface to afford easy manual access to the sheets 12 as may be needed to use the pad assembly 10.

Preferably the band 18 of repositionable pressure sensitive adhesive that extends parallel to the first edge 15 is continuous, and has a width in a direction normal to the first edge 15 in the range of 3.75 to 6.25 centimeters (1.5 to 2.5 inches), with that band 18 preferably being about 5 centimeter (2 inches) wide. Alternatively, however, the band 18 of repositionable pressure sensitive adhesive could comprise a plurality of spaced areas coated with pressure sensitive adhesive that also has a width in a direction normal to the first edge 15 in that range.

While the repositionable pressure sensitive adhesive used to form the band 18 could be of the type used on "Post-it" brand notes that is described in U.S. Pat. No. 3,691,140, the content whereof is incorporated herein by reference, preferably the repositionable pressure sensitive adhesive is an adhesive containing collapsed hollow microspheres of the type described in U.S. patent application Ser. No. 276,767 filed Nov. 30, 1988 now U.S. Pat. No. 5,045,569 the content whereof is incorporated herein by reference. Briefly, the hollow microspheres in the adhesive are predominantly iso-octyl acrylate, with a minor portion of a more polar comonomer, and are polymerized in generally spherical shapes with small fluid filled inclusions. When the adhesive is coated on the sheets 12 to form the bands 18, the fluid

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filling the inclusions evacuates, and the microspheres collapse as they dry compared to solid microspheres which dry to a more or less spherical shape. When dry, the hollow collapsed microspheres in the adhesive are pancake like in shape. Preferably, the pressure sensitive adhesive in the bands 18 comprises hollow collapsed microspheres consisting of a 94/6 ratio of iso-octyl acrylate to acrylic acid with diameters of about 60 microns. The adhesive containing the hollow collapsed microspheres provides advantages compared to adhesives containing solid microspheres. The hollow collapsed microspheres adhere well to the sheets 12 without the use of special primers so that few of the collapsed microspheres will transfer from the sheets 12 to a surface to which the sheets 12 are temporarily adhered by the bands 18 of adhesive. Also, the hollow collapsed microspheres provide relatively high adhesive shear strength. (i.e., "shear strength" is a measure of the cohesiveness or internal strength of an adhesive. That internal strength is measured by determining the amount of force required to pull an adhesive coated strip or sheet from a standard flat surface in a direction parallel to that surface to which the adhesive on the strip has been affixed with definite pressure, and is measured in time required to pull a standard area of adhesive coated material from that surface under the stress of a constant, standard load). The shear strength of the preferred adhesive containing the hollow collapsed microspheres is significantly greater than that needed for good adhesion to smooth wall surfaces, and allows the sheets 12 to be removably attached for a long period of time to many wall surfaces that are irregular and/or uneven.

The portion of the front surface of each sheet 12 to which the band of adhesive 18 on the adjacent sheet is adhered to help retain the sheets 12 in the stack 17 is coated with a layer 38 of a suitable back sizing material (see FIG. 3) to provide a desired releasable level of adhesion between the band of adhesive 18 and the adjacent sheet 12, which back sizing material for the preferred pressure sensitive adhesive described above can be that described in U.S. Pat. No. 2,532,011, the content whereof is incorporated herein by reference.

A test was performed to compare the ability of bands 18 of the preferred adhesive described above to adhere sheets 12 to various surfaces compared to sheets of the same size adhered with the same sized bands of the adhesive used on "Post-it" brand notes and the bands of adhesive on the sheets from the "Clingers" brand note pad assembly commercially available from the Ampad Corporation that is described above. The surfaces to which the test sheets were adhered were those of painted metal and painted sheet rock which were both very smooth, the surface of the fabric commonly used on modular partitions sold by the Steelcase Office Furniture Company, Grand Rapids, Mich., which is commercially designated "Aria" by that company and which is relatively rough compared to fabric used in wearing apparel but relatively smooth compared to many other fabrics used to cover walls, and the surface of a porous concrete block that had many deep pits on an otherwise fairly flat surface and had been painted. The results were as follows:

| Sample | Painted | | | |
|-------------|---------------|------------|----------------|------------------------|
| | Painted Metal | Sheet rock | Cubicle Fabric | Painted Concrete Block |
| Sheets from | 4+ days | 3-4 days | 1 minute | 1-1.5 minutes |

-continued

| Sample | Painted Metal | Painted Sheet rock | Cubicle Fabric | Painted Concrete Block |
|---|---------------|--------------------|----------------|------------------------|
| Ampad's "Clingers" pad assembly | | | | |
| Sheets having bands of the adhesive used on "Post-it" brand notes | 4+ days | 4+ days | 20-30 min. | 10-15 min. |
| Sheets 12 with bands of the preferred adhesive described above | 4+ days | 4+ days | 4+ days | 3-7 days |

As can be seen from these test results, sheets 12 with bands 18 of the preferred adhesive containing collapsed hollow microspheres that is described above hung for long periods of time on either rough or smooth surfaces. On the cubicle fabric, they hung for over four days compared to only one half hour for the next best sample. On painted concrete, the toughest surface to stick to due to reduced surface contact, the sheets with bands 18 of the preferred adhesive containing collapsed hollow microspheres hung at least three days compared to less than fifteen minutes for the next best sample.

After writing on the front surface of the top sheet 12 in the pad assembly if he chooses to do so, a user of the pad assembly 10 can peel the band of adhesive 18 on that top sheet 12 away from the second sheet 12 in the pad assembly 10 by pulling on the top sheet 12 adjacent its second edge 16 in a direction generally at a right angle to the front surface of the underlying sheet 12. Tension in the top sheet 12 caused by such pulling will progressively peel the band 18 of adhesive from the underlying sheet 12, and the user will feel the top sheet 12 move much more easily away from the underlying sheet 12 as the last portion of the band 18 separates from the underlying sheet 12, thereby providing the user with a tactile signal that he should stop pulling on the sheet 12 if he does not wish to separate the top sheet 12 from the pad assembly 10. If the user does not wish to remove the top sheet 12 from the pad assembly 10, he can then stop pulling on the sheet and bend the top sheet 12 back over the support edge 26 on the top portion 24 of the back card 22, whereupon the layer 20 of padding compound will bend between the top sheet 12 and the underlying sheet 12 completely exposing the front surface of the underlying sheet while the layer 20 of padding compound remains adhered to the top sheet supported over the support edge 26. If the user wishes to remove the top sheet 12 from the pad assembly he can simply peel its first edge 15 away from the layer 20 of padding compound from which the top sheet will separate cleanly leaving a smooth first edge 15 on the separated sheet 12, whereupon the user may releasably adhere the removed sheet to a vertical support surface using the band 18 of pressure sensitive adhesive. After the uppermost sheet 12 is either bent back over the support edge 26 or removed, a user may similarly peel away each successive underlying sheet 12 and either also bend it back over the support edge 26 or remove it from the pad assembly 10. Subsequently, if desired, the user can reposition any sheets 12 bent back over the support edge 26 in their original position on the pad and

re adhere them to the underlying sheet 12 on the pad using the bands 18 of adhesive. Also, a user can remove a number of sheets 12 from the pad assembly while leaving them adhered together, whereupon the user can adhere those removed sheets to a surface using the band 18 of adhesive on the bottom most sheet 12 so that the user now in effect has two pad assemblies from which individual sheets 12 can be peeled away and treated in the manners described above. The bands 18 of adhesive will provide good adhesion to even rough vertical support surfaces, such as those of cloth or painted cement blocks, while affording clean removal of the sheets from all surfaces without leaving adhesive residue or damaging the surface such as by removing paint, paper, or fabric from the surfaces.

As an alternative to including only the stack 17 of sheets 12, if desired, the pad assembly according to the present invention can further include a second stack 40 of sheets as is illustrated in dotted outline in FIG. 2, which second stack 40 includes sheets identical to the sheets 12 attached together by bands of repositionable pressure sensitive adhesive (not shown) and a layer of padding compound (not shown) disposed in the same locations and serving the same functions in the second stack 40 as the bands 18 of repositionable pressure sensitive adhesive and the layer 20 of padding compound serve on the stack 17 of sheets 12 attached to the front surface of the the back card 22. The second stack of sheets is attached to the rear surface of the back card 22 in a position generally opposite the stack 17 of sheets 12 attached to the front surface of the back card 22.

The present invention has now been described with reference to one embodiment thereof. It will be apparent to those skilled in the art that many changes can be made in the embodiment described without departing from the scope of the present invention. For example, pads having some of the claimed structural combinations with sizes similar to those of conventional pads of "Post-it" brand notes available from Minnesota Mining and Manufacturing Company may be useful for some purposes. Thus the scope of the present invention should not be limited to the structure described in this application, but only by structures described by the language of the claims and the equivalents of those structures.

We claim:

1. A pad assembly comprising:

a multiplicity of flexible sheets, each sheet being generally of the same size, having front and rear surfaces, having peripheral edges including first and second opposite edges, having a band of repositionable pressure sensitive adhesive coated on said rear surface adjacent to and spaced by a small predetermined spacing from said first edge and spaced by a large predetermined spacing from said second edge, said sheets being disposed in a stack with the corresponding peripheral edges of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering that sheet to the adjacent sheet in the stack; and

a layer of padding compound disposed over and releasably adhered to the aligned first edges of the sheets in the stack, said padding compound being sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear

surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets, and said layer of padding compound being sufficiently adhered to the sheets to remain adhered to the adjacent sheets during such flexing while affording manual peeling of the one sheet from the padding compound to separate that one sheet from the stack,

said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge being at least 0.6 centimeter (0.25 inch) wide in a direction normal to said first edge and providing a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets that allows the peeling force being manually applied to be terminated and thereby restricts inadvertent separation of that sheet from the padding compound, and the said band of repositionable pressure sensitive adhesive afford removable supporting adhesion of one of the sheets separated from the stack to a vertical support surface.

2. A pad assembly according to claim 1 wherein said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge is at least 1.2 centimeter (0.5 inch) wide in a direction normal to said first edge.

3. A pad assembly according to claim 1 wherein said band of repositionable pressure sensitive adhesive is continuous, extends parallel to said first edge, and has a width in direction normal to said first edge in the range of 3.8 to 6.4 centimeters (1.5 to 2.5 inches).

4. A pad assembly according to claim 1 wherein said band of repositionable pressure sensitive adhesive comprises a plurality of spaced areas coated with pressure sensitive adhesive and extends parallel to said first edge.

5. A pad assembly according to claim 1 further including a stiff back card having a front surface, the rear surface of the bottom most sheet in the stack being attached to the front surface of the back card, and the front surface of the back card being at least coextensive with the sheets in the stack.

6. A pad assembly according to claim 1 wherein said repositionable pressure sensitive adhesive comprises hollow collapsed microspheres consisting of a 94/6 ratio of iso-octyl acrylate to acrylic acid with diameters of about 60 microns.

7. A pad assembly comprising:

a multiplicity of flexible sheets, each sheet being generally of the same size, having front and rear surfaces, having peripheral edges including first and second opposite edges, having a band of repositionable pressure sensitive adhesive coated on said rear surface adjacent to and spaced by a small predetermined spacing from said first edge and spaced by a large predetermined spacing from said second edge, said sheets being disposed in a stack with the corresponding peripheral edges of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering that sheet to the adjacent sheet in the stack; and

a layer of padding compound disposed over and releasably adhered to the aligned first edges of the sheets in the stack, said padding compound being sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets, and said layer of padding compound being sufficiently adhered to the sheets to remain adhered to the adjacent sheets during such flexing while affording manual peeling of the one sheet from the padding compound to separate that one sheet from the stack,

said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge providing a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets that allows the peeling force being manually applied to be terminated and thereby restricts inadvertent separation of that sheet from the padding compound, and the said band of repositionable pressure sensitive adhesive affords removable supporting adhesion of one of the sheets separated from the stack to a vertical support surface;

said pad assembly further including a stiff back card having a front surface, the rear surface of the bottom most sheet in the stack being attached to the front surface of the back card, and the front surface of the back card being at least coextensive with the sheets in the stack, said back card having a top portion projecting past the aligned first edges of said sheets, said top portion having a peripheral support edge generally parallel to said first edges of said sheets spaced in the range of about 5 to 10 centimeters (2 to 4 inches) from said first edges of said sheets, and said top portion having an elongate opening generally aligned with and spaced from said peripheral edge of said top portion with the part of said top portion between said opening and said support edge providing a handle for said pad assembly.

8. A pad assembly according to claim 7 wherein said sheets have a dimension between said first and second edges of about 775 millimeters (30.5 inches) and a width in a direction parallel to said first and second edges of about 580 millimeters (22.8 inches).

9. A pad assembly according to claim 7 wherein said back card has a rear surface opposite said front surface, and said pad assembly includes a second stack of sheets attached together by bands of repositionable pressure sensitive adhesive and a layer of padding compound disposed in the same location in said second stack as said bands of repositionable pressure sensitive adhesive and said layer of padding compound on said stack attached to the front surface of the said back card, said second stack being attached to the rear surface of said back card in a position generally opposite said stack attached to the front surface of said back card.

10. A pad assembly comprising:

a multiplicity of flexible sheets, each sheet being generally of the same size, having front and rear surfaces, having peripheral edges including first and second opposite edges, having a band of reposition-

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able pressure sensitive adhesive coated on said rear surface adjacent to and spaced by a small predetermined spacing from said first edge and spaced by a large predetermined spacing from said second edge, said sheet being disposed in a stack with the corresponding peripheral edges of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering that sheet to the adjacent sheet in the stack; and

a layer of padding compound disposed over and releasably adhered to the aligned first edges of the sheets in the stack, said padding compound being sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets, and said layer of padding compound being sufficiently adhered to the sheets to remain adhered to the adjacent sheets during such flexing while affording manual peeling of the one sheet from the padding compound to separate that one sheet from the stack,

said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge providing a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets that allows the peeling force being manually applied to be terminated and thereby restricts inadvertent separation of that sheet from the padding compound, and the said band of repositionable pressure sensitive adhesive affords removable supporting adhesion of one of the sheets separated from the stack to a vertical support surface;

said pad assembly further including a stiff back card having a front surface, the rear surface of the bottom most sheet in the stack being attached to the front surface of the back card, and the front surface of the back card being at least coextensive with the sheets in the stack, said back card having a top portion projecting past the aligned first edges of said sheets, said top portion having a peripheral support edge generally parallel to said first edges of said sheets spaced in the range of about 5 to 10 centimeters (2 to 4 inches) from said first edges of said sheets, and said sheets having a dimension between said first and second edges of about 775 millimeters (30.5 inches) and a width in a direction parallel to said first and second edges of about 580 millimeters (22.8 inches).

11. A pad assembly comprising:

a multiplicity of flexible sheets, each sheet being generally of the same size, having front and rear surfaces, having peripheral edges including first and second opposite edges, having a band of repositionable pressure sensitive adhesive comprising hollow collapsed microspheres of polymeric material coated on said rear surface adjacent to and spaced by a small predetermined spacing from said first edge and spaced by a large predetermined spacing from said second edge, said sheets being disposed in a stack with the corresponding peripheral edges

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of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering that sheet to the adjacent sheet in the stack; and

a layer of padding compound disposed over and releasably adhered to the aligned first edges of the sheets in the stack, said padding compound being sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets, and said layer of padding compound being sufficiently adhered to the sheets to remain adhered to the adjacent sheets during such flexing while affording manual peeling of the one sheet from the padding compound to separate that one sheet from the stack,

said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge providing a tactile feel when the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets that allows the peeling force being manually applied to be terminated and thereby restricts inadvertent separation of that sheet from the padding compound, and the said band of repositionable pressure sensitive adhesive affords removable supporting adhesion of one of the sheets separated from the stack to a vertical support surface.

12. A pad assembly comprising:

a multiplicity of flexible sheets, each sheet being generally of the same size, having front and rear surfaces, having peripheral edges including first and second opposite edges, having a band of repositionable pressure sensitive adhesive coated on said rear surface adjacent to and spaced by a small predetermined spacing from said first edge and spaced by a large predetermined spacing from said second edge, said sheets being disposed in a stack with the corresponding peripheral edges of the sheets aligned, the front and rear surfaces of adjacent sheets facing each other, and the band of repositionable pressure sensitive adhesive on each sheet adhering that sheet to the adjacent sheet in the stack; and

a layer of padding compound disposed over and releasably adhered to the aligned first edges of the sheets in the stack, said padding compound being sufficiently flexible to allow, after the band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack, that one sheet to be pivoted away from that adjacent sheet by hinge-like flexing of the padding compound between the sheets, and said layer of padding compound being sufficiently adhered to the sheets to remain adhered to the adjacent sheets during such flexing while affording manual peeling of the one sheet from the padding compound to separate that one sheet from the stack,

said small predetermined spacing between said band of repositionable pressure sensitive adhesive and said first edge providing a tactile feel when the

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band of repositionable pressure sensitive adhesive on the rear surface of one of the sheets in the stack is separated from the front surface of the adjacent sheet in the stack by manual peeling apart of the sheets that allows the peeling force being manually applied to be terminated and thereby restricts inadvertent separation of that sheet from the padding compound, and the said band of repositionable pressure sensitive adhesive affords removable supporting adhesion of one of the sheets separated from the stack to a vertical support surface; said pad assembly further including a stiff back card having a front surface, the rear surface of the bottom most sheet in the stack being attached to the

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front surface of the back card, and the front surface of the back card being at least coextensive with the sheets in the stack, said back card having a top portion projecting past the aligned first edges of said sheets, said top portion having a peripheral support edge generally parallel to said first edges of said sheets, and said top portion having two parallel elongate through slots positioned adjacent opposite sides of the back card and aligned parallel to said support edge, said slots being adapted to receive the support pegs on some types of easels on which said pad assembly might be supported.

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United States Patent [19][11] **Patent Number:** 5,194,299**Fry**[45] **Date of Patent:** Mar. 16, 1993**[54] REPOSITIONABLE PRESSURE-SENSITIVE ADHESIVE SHEET MATERIAL****[75] Inventor:** Arthur L. Fry, Saint Paul, Minn.**[73] Assignee:** Minnesota Mining and Manufacturing Company, St. Paul, Minn.**[21] Appl. No.:** 948,095**[22] Filed:** Dec. 31, 1986**Related U.S. Application Data****[60]** Division of Ser. No. 662,605, Oct. 19, 1984, abandoned, which is a continuation-in-part of Ser. No. 662,605, Oct. 19, 1984, abandoned.**[51] Int. Cl.⁵** B32B 31/00**[52] U.S. Cl.** 427/208.6; 427/421; 427/284; 427/285; 428/194; 428/198; 428/201; 428/202; 428/211; 428/343**[58] Field of Search** 428/194, 198, 211, 343, 428/40, 202, 201; 427/208.6, 421, 284, 285**[56] References Cited****U.S. PATENT DOCUMENTS**

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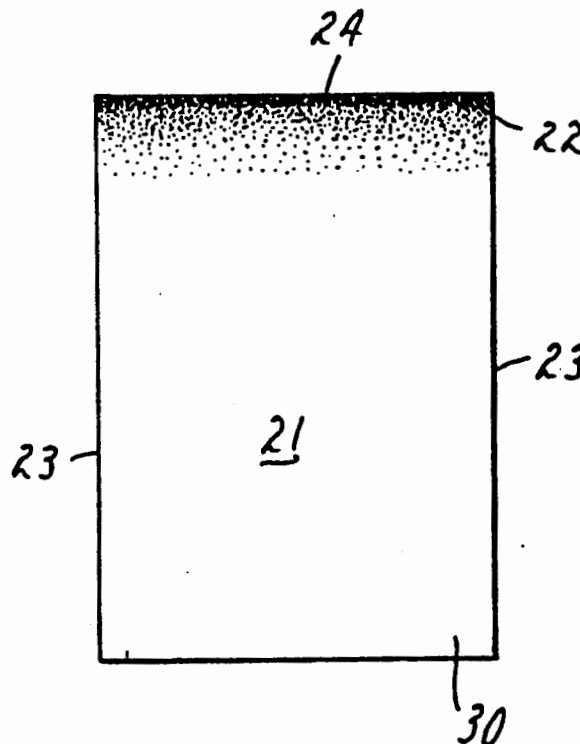
| | | | |
|-----------|---------|---------------------|-----------|
| 2,729,193 | 1/1956 | Scholl | 118/202 |
| 2,750,942 | 6/1956 | Robson | 128/156 |
| 2,940,868 | 6/1960 | Patchell | 117/38 |
| 3,033,702 | 5/1962 | Fenselau | 117/38 |
| 3,174,888 | 3/1965 | Morgan | 156/230 |
| 3,671,284 | 6/1972 | Uhrig | 117/21 |
| 3,691,140 | 9/1972 | Silver | 260/78.5 |
| 3,741,786 | 6/1973 | Torrey | 117/3.1 |
| 3,808,088 | 4/1974 | Knechiges et al. | 161/148 |
| 3,811,438 | 5/1974 | Economou | 128/156 |
| 3,857,731 | 12/1974 | Merrill, Jr. et al. | 117/122 |
| 3,900,642 | 8/1975 | Michel | 428/40 |
| 3,967,624 | 7/1976 | Milnamow | 128/287 |
| 4,004,049 | 1/1977 | Horwat et al. | 427/208.6 |
| 4,063,559 | 12/1977 | Tritsch | 128/287 |
| 4,166,152 | 8/1979 | Baker et al. | 428/522 |
| 4,460,634 | 7/1984 | Hasegawa | 428/124 |

FOREIGN PATENT DOCUMENTS

1541311 2/1979 United Kingdom .

Primary Examiner—Alexander S. Thomas*Attorney, Agent, or Firm*—Gary L. Griswold; Walter N. Kirn; Thomas J. Odar**[57] ABSTRACT**

Pressure-sensitive adhesive sheet material having the ability to be applied to paper and removed therefrom without lifting fibers or delaminating the paper. The otherwise conventional pressure-sensitive adhesive is applied to the backing by spraying, resulting in a non-repetitive pattern of adhesive islands.

5 Claims, 1 Drawing Sheet

U.S. Patent

Mar. 16, 1993

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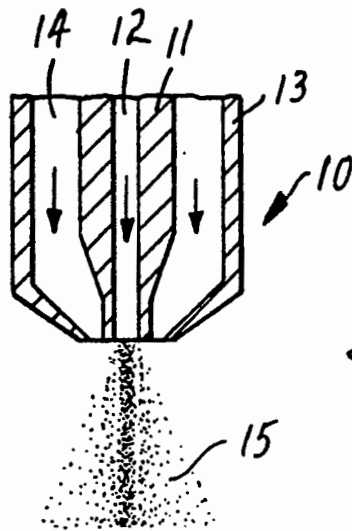


FIG. 1

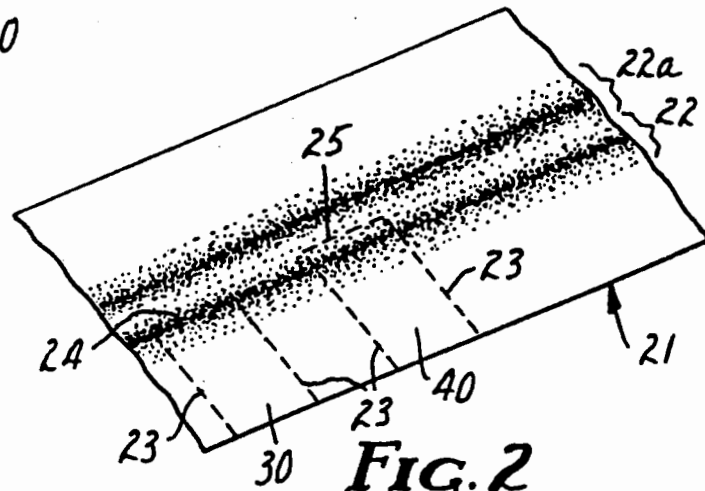


FIG. 2

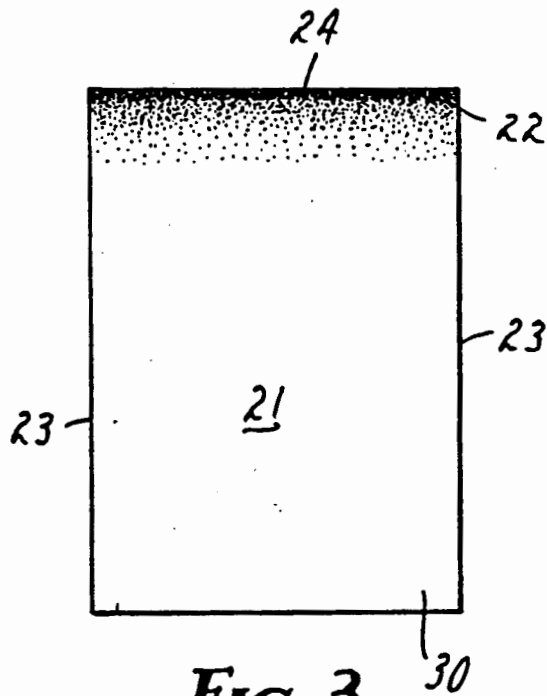


FIG. 3

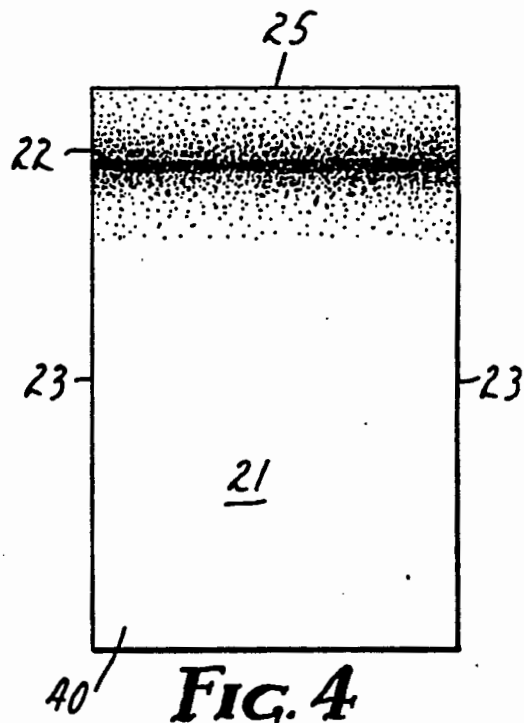


FIG. 4

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REPOSITIONABLE PRESSURE-SENSITIVE ADHESIVE SHEET MATERIAL

CROSS REFERENCE TO RELATED APPLICATION

This application is a division and continuation-in-part of Ser. No. 662,605, filed Oct. 19, 1984 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to normally tacky and pressure-sensitive adhesive sheet material and is particularly concerned with repositionable products.

In the mid-1970's applicant's assignee introduced repositionable adhesive tapes and note papers, which found an immediate acceptance and today provide a substantial volume of business. The adhesive utilized in these products, typically present in a narrow band adjacent one edge of the sheet material, consists essentially of an adhesive binder layer containing numerous infusible, solvent-dispersible tacky elastomeric microspheres that typically have a diameter of 50-75 micrometers. In another embodiment of this type of product, bulletin boards are surfaced with sheet material bearing the same repositionable adhesive, so that notices, pictures, clippings, etc. can be temporarily adhered, removed, and repositioned; see, e.g., U.S. Pat. No. 3,857,731.

Products of the type described in the preceding paragraph can be adhered to almost any substrate, including paper (even such weak paper as newsprint), readily removed without delaminating the substrate, and subsequently repositioned. The force required to peel these products from a paper substrate is maintained in the approximate range of 8 to 80 (preferably 10 to 50) grams per centimeter width; products having significantly lower peel adhesion (e.g., less than 8 g/cm width) generally lack the ability to resist inadvertent removal, often falling off. Products having significantly higher peel adhesion (e.g., more than 80 g/cm) on the other hand, tend to tear or delaminate weak papers at normal removal rates. Application of the adhesive coating so as to achieve consistent peel adhesion values requires considerable knowhow, and the adhesive compositions themselves are relatively expensive to manufacture.

Numerous attempts have been made to achieve the results obtainable with microsphere adhesives by substituting more conventional pressure-sensitive adhesives (psas), which typically have continuous-coat (100% coverage) peel adhesion values, when applied to untreated paper, on the order of 100-1000 g/cm. width. (Representative adhesion values include the following: matte finish acetate tape, 107 g/cm; masking tape, 227 g/cm; book repair tape, 443 g/cm; package sealing tape, 830 g/cm; filament tape, 937 g/cm.) One approach has been to use a psa having inherently low tack, but it has been found difficult, if not impossible, to maintain consistent peel adhesion values, the nature of the note paper backing and the thickness of the adhesive layer both profoundly affecting performance. Another approach has been to apply a thinner coating than normal, it being recognized that this will reduce peel adhesion. Unfortunately, however, it is almost impossible to prepare consistent coatings having removal values in the 10-50 g/cm range; even when this can be done, adhesion will frequently increase upon extended contact to a degree sufficient to cause tearing or delamination upon attempted removal.

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Others have tried to obtain the desired degree of adhesion by locally deactivating portions of a full coating of a psa, as taught in U.S. Pat. No. 2,515,423, but this technique has likewise proved difficult to control. The same problems are encountered in attempting to locally mask portions of a full coating of a psa, as taught in U.S. Pat. Nos. 1,944,834, 2,000,475, 3,900,642, 3,967,624, and 4,063,559, as well as in British Patent No. 1,541,311.

The prior art has also suggested applying pressure-sensitive adhesive to only portions of a backing, leaving other portions free from adhesive. Thus, it has been proposed to make spaced adhesive stripes extending in either the machine direction (U.S. Pat. No. 2,349,709) or the cross direction (U.S. Pat. Nos. 2,386,731 and 3,811,438), as well as products having spaced adhesive spots (U.S. Pat. Nos. 3,174,888 and 3,741,786). By and large, however, the spots were so large that attempted removal of the tape from newsprint will cause tearing or delamination. Prior to the present invention, then, it is believed that there has never existed a product having performance equivalent to that of the microsphere adhesives referred to above, but made with conventional pressure-sensitive adhesives.

BRIEF SUMMARY

The present invention provides a removable and repositionable adhesive product* comprising a substrate (especially sheet material such as paper) bearing on one surface a discontinuous non-repetitive** adhesive coating comprising first areas where psa is exposed and second areas where psa is not exposed. The psa is sufficiently adherent to newsprint that if sheet material having a continuous coating of the psa is applied to sheet backing in the normal manner and the adhesive surface then placed in contact with a sheet of newsprint, it cannot be peeled away at normal rates (e.g., 10-15 cm/sec) without delaminating the newsprint. The invention is based on the application of conventional pressure-sensitive adhesives to a substrate in certain critical patterns where discrete spaced areas of adhesive are carefully controlled as to size, thickness, and percentage of substrate covered. The resultant product is not only simple and economical to manufacture but also offers the first practical alternative to the use of the tacky microsphere adhesives.

* The term "removable and repositionable" is intended to refer not only to products which can be temporarily adhered to, removed from, and repositioned on paper sheets but also to products to which paper sheets can be temporarily adhered, removed, and repositioned.

** The term "non-repetitive" means that the adhesive pattern is random, as opposed to the repeating pattern obtained by using a rotogravure roll or other printing equipment.

More specifically, it has been found that the adhesive used in practicing the invention should cover about 10 to about 85% (preferably about 20 to about 60%) of the area over which adhesive is applied. Individual adhesive "islands" should be about 0.01-0.15 mm (preferably about 0.02-0.10 mm) thick and at least roughly circular, having a diameter no greater than 0.02-1.5 mm (preferably on the order of 0.05-0.08 mm). In some instances adjacent islands may join together to form a short chain or larger island, provided that at least one dimension does not exceed the stated limits. Within the limits specified, the numerical values are interrelated, depending also on the tackiness of the specific adhesive employed. To illustrate, an extremely tacky adhesive should be so applied that it is present in smaller islands or a thinner coating, or occupies a lower percentage of the backing, than a less tacky adhesive. The adhesive can be applied as from an aqueous dispersion or a solution in organic

solvent, or perhaps as either a hot melt or a thick monomeric syrup that is thereafter polymerized in situ, e.g., as taught in U.S. Pat. No. 4,181,752. Even where aqueous dispersions (which are presently preferred) are applied to a paper backing, there is usually no evidence of irregular shrinking, distortion, or cockling. Coating and drying or curing procedures for "island"-coated adhesives are faster, require less energy, result in lower paper distortion, and use less adhesive than for full-coated adhesives. The resultant adhesive sheet material can be adhered to paper, allowed to remain in contact therewith for two weeks at room temperature and then removed without visibly damaging the paper. Preferred embodiments of the invention display the same peel removal force of 10-50 g/cm characteristic of microsphere adhesives, enabling them to be adhered to newspaper for extended periods of time without delaminating it upon removal.

A further embodiment of the invention includes a sheet backing or other substrate in which the population density of the adhesive islands in the discontinuous coating varies, e.g., from low at one edge of the coating pattern and high at the other or low at both edges and high in the central portion. When such a pattern is provided at the edge of a sheet of paper, so that the population density of the adhesive islands is lowest adjacent the uncoated portion of the sheet, the sheet will remain flat when it is applied to a substrate, removed, and replaced. This highly desirable performance feature is frequently not found in conventional products. For all papers, there is some adhesion force that will cause the paper to curl when a note is pulled away from a surface at an angle of 90° or greater. With a tapered adhesion profile, there is always a part of the adhesive that is too low in adhesion to curl the paper, but high enough to hold the curled portion down when it is readhered.

The desirable results described above are attained by the simple but highly unconventional process of spraying the adhesive onto the sheet backing. When adhesive is applied from a spray head in fixed position above a moving web of paper, a strip of discontinuous adhesive, perhaps 1-2.5 cm wide, is applied; masks may be employed to keep overspray from other areas. Typically the edges of the adhesive strip have a lower population density than does the center. This effect is caused by the inherent characteristics of the spray pattern emanating from a spray head, where the spacing between droplets is least at the center, gradually increasing radially outward therefrom.

BRIEF DESCRIPTION OF THE DRAWING

Understanding of the invention will be enhanced by referring to the accompanying drawing, in which like numbers refer to like parts in the several views, and in which:

FIG. 1 is a vertical cross-sectional view of a spray head, showing the distribution of particles emanating therefrom;

FIG. 2 is a perspective view of a sheet that has been provided with two stripes from spaced adhesive spray heads;

FIG. 3 is a plan view of the rear surface of a sheet that has been provided with a sprayed adhesive strip adjacent one edge; and

FIG. 4 is a plan view of the rear surface of a sheet similar to that of FIG. 3 except that the distribution of adhesive islands is different.

DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS

In the drawing, spray unit 10 includes nozzle 11, having central channel 12, through which adhesive is supplied. Surrounding nozzle 11 and spaced radially therefrom is air cap 13, defining an annular passage through which air is supplied. As the adhesive emerges from channel 12, the annular air stream emitted from channel 14 breaks the adhesive into a cloud of small droplets 15. The pattern assumed by droplets 15 is generally circular, the greatest concentration being at the central portion, gradually decreasing to zero at the periphery. The diameter of the spray pattern is directly related to the distance between spray unit 10 and the substrate toward which adhesive droplets 15 are directed. The size of droplets 15 can be altered by appropriately adjusting spray unit pressures, and the coating weight applied to a moving substrate can be adjusted by varying either the rate at which the spray is applied or the speed at which the substrate moves. Thus, the application of a pressure-sensitive adhesive with a spray unit offers great versatility in the coating applied. Speaking in general terms, adhesive islands having smaller diameter but greater thickness can be obtained by spray coating than by printing.

For purposes of the invention, it is important that the adhesive droplets be small, e.g., on the order of 0.02 to 0.2 mm in diameter. Larger droplets result in an adhesive coating that not only tends to cause "raspy," or erratic, removal of a coated sheet from a paper substrate but also is more likely to pull paper fibers. It is much easier to produce articles coated with small adhesive "islands" by spray techniques than by conventional printing methods. It is also far easier to apply adhesive droplets in a close-spaced pattern by spray coating than by printing methods. Further, printed patterns are difficult to maintain consistently, since the application of adhesive is affected by wear of the printing roll, as well as by the unavoidable consequence of having dried adhesive or other contaminants fill in part of the cells on a rotogravure roll or the holes in a screen. It is easy to distinguish a sprayed pattern from a roll coated or printed pattern, since the latter two are repetitive, and the sprayed pattern is not.

Another consideration is the fact that spray equipment is considerably less expensive than printing equipment. Additionally, since the spray head does not contact the substrate to be coated, articles that are fragile or have irregular surfaces may be coated, whereas printing methods, especially at high speeds, cannot be effectively employed in this manner. Thus the present invention enables the preparation of note pads, labels, paper napkins, and other items that require low adhesion levels and removability.

Spray unit 10 may be of any of several types, including the so-called airless spray head. For commercial application, however, it is most practical to use spray heads that do not require frequent cleaning.

FIG. 2 shows a portion of a web 21 that has been adhesive-coated using a pair of spray heads 10 to apply a pair of adhesive stripes 22 and 22a extending along the machine direction of web 21. Consistent with the spray pattern shown in FIG. 1 and discussed above, the population density of adhesive droplets 15 is highest at the center of stripes 22, 22a, gradually decreasing as the distance from the center increases. By die-cutting along dotted lines 23, 24 or 23, 25 shown in FIG. 2, one can

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then obtain removable repositionable notes 30, 40 of the type shown, respectively, in FIGS. 3 and 4. It will be observed that in each case the population density of adhesive droplets in adhesive strips 22 is lowest immediately adjacent the uncoated part of note 30 or 40, leading to an interesting advantage when the note is either removed from a pad of such notes or applied to a substrate, removed, and subsequently reapplied. When the user of note 30 or 40 removes it, typically at an angle of 90°-180°, there will be some point where the population density of the adhesive islands is high enough that the note will deform or curl, adhesive side out, along the line of greatest population density of the adhesive islands. When the note is then applied or reapplied to a substrate, the less densely populated portion of the adhesive strip 22 serves to rebound the note in a flat position. In contrast, conventionally coated notes remain curled when reapplied, causing an unsightly appearance and increasing the likelihood that they will snag on overlying sheets of paper and possibly be removed inadvertently. Others have attempted to cope with this problem by coating adhesive strips in which the edge adjacent the uncoated portion of the note has a saw-tooth pattern; although effective to a degree, this technique increases the difficulty of applying the adhesive strip.

Note 30 is obtained by cutting along the densest central portion of adhesive strip 22. If desired, however, note 40 may be obtained by cutting along the opposite edge of adhesive strip 22, where the density of the adhesive islands is also low. One advantage of the product of FIG. 4 is that there is a reduced tendency for the cutting equipment to become gummed up with adhesive during the process of manufacture.

It will be recognized that if desired, spray units 10 could be so positioned above a moving web as to achieve an adhesive coating of substantially the same non-repeating pattern over whatever portion of the web it is desired to coat.

As an aid to understanding and practicing the invention, various measuring and testing techniques employed will now be described.

Percent Adhesive Coverage

The adhesive islands are first identified by rubbing black artists' charcoal into the surface of a soft rubber sheet and then pressing the adhesive onto the blackened surface, using a 3.8-cm diameter rubber roller to ensure intimate contact. The charcoal adheres to the surface of the adhesive areas but does not adhere to the uncoated portions of the paper backing. Using obliquely directed light, an image analyzing device, such as the Cambridge "Imanco" Image Analyzer No. 720, is then used to examine 16 fields, each 5 mm × 5 mm, in the densest part of the spray pattern and the 16 readings averaged.

Droplet Size Measurement

The adhesive-coated surface is examined using a 100-power microscope having an optical comparator grating. Adhesive islands can be viewed and measured directly.

Thickness Measurements

Strips approximately 1 mm wide are cut from the adhesive-coated sheet material, bent into a V shape, and positioned edgewise on the stage of the microscope used for width measurements. The height of the adhesive

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islands above the surface of the paper backing can be measured directly.

Peel Adhesion

The adhesive to be tested is first applied to a surface to which it will adhere tenaciously, e.g., anodized aluminum or alumina-surfaced biaxially oriented polyester film such as that described in U.S. Pat. No. 4,190,321. A 2.54-cm × 25.4-cm strip of 25 micrometer biaxially oriented polyethylene terephthalate film is then applied to the adhesive surface and rolled down with two passes of a 2-kg roller. Using a tensile testing machine, the force required to pull the polyester strip from the adhesive surface at a 90° angle at a rate of 30.5 cm per minute is then determined. Peel adhesion tests are run both immediately after sample preparation and after a specified delay that allows the adhesion bond to stabilize.

Delamination Strength

To determine the delamination strength of various types of paper, a 2.54-cm strip of 25-micrometer polyester film having a full coating of acrylate-based pressure-sensitive adhesive is placed in contact with the surface of the paper and rolled down with two passes of a 2-kg roller. The adhesive-coated strip is then pulled away from the paper at a 90° angle at a rate of 30.5 cm per minute. (It is, of course, necessary to use tape having an adhesion to the paper being tested greater than the delamination strength of the paper itself). It is interesting to note that the force required to initiate tearing or delamination of the paper is greater than the steady-state force required to continue tearing or delamination after it has occurred. This phenomenon may show why a discontinuous adhesive coating on the tape product permits its removal from a paper surface without delamination, even at forces that would cause delamination if the adhesive coating were continuous. Although a discontinuous adhesive coating may pull loose other individual fibers (which are typically 4-5 mm long and 0.01-0.03 mm in diameter), there is insufficient contact between any given adhesive island and the several adjacent fibers to permit the initial delamination to occur. In this regard, it has been found that the shape of the adhesive islands has an effect on their tendency to initiate tearing. For example, circular adhesive islands are less likely to tear paper than parallel linear adhesive islands whose width is the same as the diameter of the circular islands, especially when removal forces are exerted parallel to their long dimension.

Using the test just described, the force required to initiate tearing or delamination and the force required to continue delamination or tearing that was previously commenced for several types of paper are, respectively, as follows: manila file folder, 341 g/cm, 309 g/cm; wood-free No. 4 sulfite typewriter bond weighing 4.68 g/m², 297 g/cm, 116 g/cm; newsprint, 177 g/cm, 79 g/cm.

In the following illustrative but non-limiting examples, all parts are by weight unless otherwise noted.

EXAMPLE 1

The adhesive employed in this example was a 57% solids high-tack aqueous isoamylacrylate emulsion, commercially available from Rohm & Haas under the registered trademark "Rhoplex" N619. This adhesive was applied under a pressure of about 50 kPa to an air atomizing gun (Model CFA 700, available from A. C. Wallberg Company), air being supplied so as to dis-

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pense adhesive droplets in a conical spray pattern, the diameter of the cone being approximately 15 cm at a distance of 20 cm from the nozzle. A web of wood-free forms bond paper weighing 4.68 g/m² was passed beneath the spray gun at a distance of about 20 centimeters at a rate of approximately 90 meters per minute, after which the sprayed web was dried in a circulating air oven at about 50° C., for about 5 seconds, and a 10-cm wide strip, occupying the central part of the spray pattern, was used for further testing. A pattern this wide might be useful for coating tape and label products, gangs of spray heads making it possible to coat extremely wide webs. To obtain a narrower width spray pattern, the spray head may be positioned closer to the web. The paper was found to be substantially uniformly covered with adhesive islands occupying 27.5% of the coated area. The diameter of the islands was about 0.05 to 0.07 mm, the thickness ranging from 0.01 to 0.05 mm. The adhesion to aluminum oxide-surfaced 100-micrometer polyester film was 29.5 g/cm, and the adhesive-coated paper could be applied to newsprint, rolled down firmly, allowed to remain in place for two weeks, and removed without tearing or delaminating the newsprint. When a control was prepared by applying a full coat of the same adhesive, about 0.3 mm thick, to the bond paper backing, the peel adhesion to aluminum oxide-surfaced polyester film was about 325 g/cm width. When applied to newsprint, the full-coated product could not be removed without causing delamination; indeed, it could not be removed from even good quality bond paper without causing the paper to tear or delaminate.

In the tabulated examples that follow, certain abbreviations are used to characterize the adhesives. For convenience in reference, these abbreviations are shown below:

| Abbreviation | Type of Pressure-Sensitive Adhesive |
|--------------|---|
| IAA | High-tack aqueous isoamylacrylate emulsion, commercially available from Rohm & Haas under the registered trademark designation "Rhoplex" N619. |
| NBA | Aqueous N-butylacrylate emulsion, commercially available from Rohm & Haas under the registered trademark designation "Rhoplex" N580. |
| LC67 | Aqueous 98:2 n-butylacrylate:hydroxymethacrylate emulsion commercially available from Rohm & Haas under the registered trademark designation "Rhoplex" LC 67 |
| UI73 | Aqueous n-butylacrylate emulsion commercially available from Union Carbide under the registered trademark designation "Ucar" 173 |
| IAMS | Aqueous 92:4:3:1 isooctylacrylate:acrylic acid:methyl methacrylate:styrene emulsion, of the type described in Ulrich U.S. Pat. Re. 24,906. |
| IOA:AA | 10% heptane solution of 95.5:4.5 isooctyl acrylate:acrylic acid copolymer of the type described in Ulrich U.S. Pat. Re. 24,906 |
| RRS | 19.8% heptane solution of 100 parts pale crepe natural rubber, 1 gram alkylated polyhydroxyphenyl (commercially available from Monsanto Chemical Company under the registered trademark designation "Santovar" A), and 75 grams of polyterpene resin (e.g., the resin commercially available from Crosby Chemicals under the registered trademark |

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-continued

| Abbreviation | Type of Pressure-Sensitive Adhesive |
|--------------|--|
| RRE | designated "Croturez" B115 or KK-187) Homogeneous blend of, on a dry weight basis, 100 parts natural rubber latex (e.g., the 62.4% solids rubber latex commercially available from Firestone Tire and Rubber company under the registered trademark designation "Hartex 103"), 25 parts carboxylated SBR emulsion (e.g., the 50.5% solids SBR emulsion commercially available from Polysar Ltd. under the registered trademark designation "Polysar" XE 222), 146 parts aliphatic hydrocarbon emulsion (e.g., the 55.0% solids emulsion commercially available from Hercules Inc. under the registered trademark designation "Piccopale" 85), and 46.9 parts acid-stable emulsion of pentaerythritol ester of hydrogenated rosin (e.g., the ester commercially available from Hercules Inc. under the registered trademark designation "Pentalyn" H). |
| S6574 | Blend of, on a weight basis, 100 parts polymethyl diphenyl siloxane containing 12% phenyl (e.g., a 30% solids solution of silicone pressure-sensitive adhesive commercially available from General Electric Company under the registered trademark designation "Silgrip" PSA 6574) and 20 parts of as 10% solution of benzoyl peroxide. After coating, the adhesive was dried two minutes at 90° C. and cured an additional two minutes at 165° C. |
| S280A | Identical to S6574 except that polydimethyl siloxane (e.g., the adhesive available from Dow Corning under the trade designation 280A), was substituted for the polymethyl siloxane. |

In order to control the adhesive island thickness in the examples, adhesive emulsions are thinned with suitable amounts of water and adhesive solutions with an appropriate solvent.

Air atomizing heads, airless spray guns, electrostatic heads, and ultrasonic heads can all be employed to create adhesive patterns in conformance with the teachings of the invention. The airless spray gun produces a flow of particles in larger drops than those obtained from air atomizing guns, and less overspray results. Among the suitable airless spray guns are Model W280, available from Wagner Spray-Tech Corporation; and Model 226-153 Series K Hydrospray, available from Binks. With all spray equipment, the relative motion between the spray head and the substrate must be sufficiently rapid to deposit discrete droplets that do not cover the entire surface when dried.

The following table, which incorporates various comparative examples in which (except as other wise noted) the adhesive was applied by spray techniques, illustrates several embodiments of the invention. In most cases, the adhesive was applied from an aqueous dispersion, permitting the use of high percentages of solids at low viscosity, allowing easier cleanup, and avoiding air pollution during drying; in other cases, however, the adhesive was applied from a solution in organic solvents. It will be seen that the results achieved depend on an interrelationship of the type of adhesive (or adhesive blend), the dimensions of the adhesive-coated areas, and the percent of the coated area which is actually occupied by adhesive.

TABLE I

| Example | ADHESIVE | | Backing | Coating Method | % Area Coated | Adhesive Island Dimensions, mm | | Peel Adhesion, g/cm |
|---------|----------|-----------------------------------|----------------------|----------------|---------------|--------------------------------|-----------|---------------------|
| | Type | 100% Coverage Peel Adhesion, g/cm | | | | Diameter | Thickness | |
| 1* | NBA | 205 | Polyester Film | Air Spray | 7 | 0.05-1.0 | 0.03-0.06 | 3 |
| 2 | " | " | " | " | 38 | " | " | 16 |
| 3 | " | " | " | " | 66 | " | " | 47 |
| 4 | " | " | " | Airless Spray | 45 | 0.07-0.6 | 0.01-0.06 | 50 |
| 5 | " | " | " | " | 60 | " | " | 49 |
| 6* | " | " | " | " | 63 | " | " | 85 |
| 7* | S280A | 246 | Paper | Air Spray | 12 | 0.2-1.0 | <0.01 | 2 |
| 8 | " | " | " | " | 22 | " | " | 11 |
| 9 | " | " | " | " | 26 | " | " | 22 |
| 10 | S280A | 246 | Paper Polyester Film | " | 54 | " | " | 38 |
| 11 | " | " | " | " | 14 | " | " | 38 |
| 12 | " | " | " | " | 26 | " | " | 41 |
| 13* | IAA | 325 | " | " | 5 | 0.05-1.0 | 0.01-0.03 | <2.0* |
| 14 | " | " | " | " | 20 | " | " | 13 |
| 15 | " | " | " | " | 28 | " | " | 30 |
| 16 | " | " | " | " | 41 | " | " | 47 |
| 17 | " | " | " | Airless Spray | 33 | 0.07-0.6 | 0.01-0.6 | 39 |
| 18 | " | " | " | " | 65 | " | " | 69 |
| 9* | S6574 | 346 | Poly. Film | Air Spray | 11 | 0.02-0.4 | 0.01 | 79 |
| 20 | " | " | " | " | 14 | " | " | 13 |
| 21 | " | " | " | " | 25 | " | " | 35 |
| 22* | " | " | " | " | 30 | " | " | 92 |
| 23 | " | " | Paper | " | 18 | " | " | 2 |
| 24 | " | " | " | " | 43 | " | " | 6 |
| 25 | RRE | 469 | " | " | 37 | 0.1-0.5 | 0.01-0.03 | 22 |
| 26 | " | " | " | " | 49 | " | " | 30 |
| 27* | " | " | " | " | 61 | " | " | 101 |
| 28 | " | " | " | " | 62 | " | " | 69 |
| 29* | " | " | " | " | 63 | " | " | 104 |
| 30* | IAMS | 180 | Polyester Film | " | 86 | 0.02-0.4 | 0.01 | 125 |
| 31 | " | " | " | " | 81 | " | " | 70 |
| 32 | " | " | " | " | 71 | " | " | 44 |
| 33 | " | " | Paper | Syringe** | 14 | 1.2-1.5 | 0.2 | 60 |
| 34 | " | " | " | " | 23 | 1.5-2.2 | 0.1 | 77 |
| 35 | " | " | " | " | 28 | 1.5-2.0 | 0.12-0.15 | 96 |

*Comparative Example

How adhesive island dimensions affect adhesion is described in the following test:

Newsprint Fiber Picking

Ordinary wire window screen (about 4 openings per running centimeter) is dipped into the adhesive to be evaluated, removed and positioned above a sheet to be coated. A jet of air is then passed over the screen, blowing the adhesive, which is held in the mesh by surface tension, onto a sheet of bond paper. A fairly wide size range of adhesive islands is thereby generated. After the adhesive has dried, a sheet of newsprint is placed over the adhesive-coated surface and forced into intimate contact with the individual adhesive areas, using a sharp-edged plastic squeegee. After 24 hours, the news-

print is removed from the adhesive-coated surface, which is then dusted with black toner powder, the powder adhering to the adhesive particles except for those areas where the adhesive is covered by paper fiber. Since the paper fibers are essentially white, the fiber-covered areas stand out in sharp contrast to those covered with black toner powder. Adhesive areas of the various size ranges are then examined closely to determine the number of areas of a given diameter to which paper fibers are attached. Generally speaking, it has been concluded that if more than 50% of the adhesive areas of any given size remove paper fibers from the newsprint, the particle size is too large. The following table shows the interrelationship of adhesive type, adhesive area dimensions, and fiber picking tendencies.

TABLE II

| Example | Adhesive | | Adhesive Island Dimensions, mm | | % Fiber Picking |
|---------|----------|-----------------------------------|--------------------------------|-----------|-----------------|
| | Type | 100% Coverage Peel Adhesion, g/cm | Diameter | Thickness | |
| 39 | U173 | 100 | 0.2 | 0.04 | 10 |
| 40 | " | " | " | 0.07 | 10 |
| 41 | " | " | 0.7 | 0.04 | 50 |
| 42 | " | " | " | 0.06 | 50 |
| 43 | " | " | " | 0.07 | 100 |
| 44 | " | " | 1.0 | 0.03 | 50 |
| 45 | " | " | " | 0.04 | 50 |
| 46 | " | " | " | 0.06 | 100 |
| 47 | " | " | 1.5 | 0.03 | 80 |
| 48 | LC67 | 224 | 0.05 | 0.06 | 15 |
| 49 | " | " | 0.1 | 0.04 | 0 |
| 50 | " | " | " | 0.07 | 15 |
| 51 | " | " | 0.3 | 0.03 | 0 |
| 52 | " | " | " | 0.04 | 20 |
| 53 | " | " | " | 0.08 | 70 |

TABLE II-continued

| Example | Type | Adhesive | | Adhesive Island Dimensions, mm | | % Fiber Picking |
|---------|-------|---------------|---------------------|--------------------------------|-----------|---|
| | | 100% Coverage | Peel Adhesion, g/cm | Diameter | Thickness | |
| 54 | " | " | " | 0.5 | 0.04 | 50 |
| 55 | " | " | " | " | 0.05 | 70 |
| 56 | " | " | " | " | 0.09 | 100 |
| 57 | " | " | " | 0.7 | 0.15 | 100 |
| 58 | " | " | " | 1.0 | 0.04 | 50 |
| 59 | " | " | " | " | 0.05 | 50 |
| 60 | " | " | " | " | 0.1 | 100 |
| 61 | S280A | 246 | " | 0.2-1.0 | <0.01 | 0 |
| 62 | " | " | " | 1.5 | 0.01 | 90 |
| 63 | S6574 | 346 | " | 0.2-0.4 | " | 0 |
| 64 | " | " | " | >1.0 | " | 90 |
| 65 | RRE | 469 | " | 0.1-0.3 | 0.03 | 0 on 30% coverage 80 on 80% coverage |
| 66 | " | " | " | 0.1-0.5 | 0.01 | 0 |
| 67 | IAA | 500 | " | 0.05 | 0.04 | 0 |
| 68 | " | " | " | 0.1 | 0.06 | 15 |
| 69 | " | " | " | " | 0.07 | 15 |
| 70 | " | " | " | 0.3 | 0.03 | 0 |
| 71 | " | " | " | " | 0.04 | 20 |
| 72 | " | " | " | " | 0.08 | 70 |
| 73 | " | " | " | 0.5 | 0.04 | 50 |
| 74 | " | " | " | 0.05 | 0.05 | 70 |
| 75 | " | " | " | " | 0.09 | 100 |
| 76 | " | " | " | 0.7 | 0.15 | 100 |
| 77 | " | " | " | 1.0 | 0.04 | 50 |
| 78 | " | " | " | " | 0.05 | 50 |
| 79 | " | " | " | " | 0.10 | 100 |

EXAMPLE 80

A DeVilbiss AGB Series 501 air atomizing spray unit having an AV 15FX nozzle and a No. 48 aircap was mounted 30 cm above a web of 20 lb. (34 g/m²) forms bond paper, which was moved at 45 m/sec. Using an atomizing air pressure of 20-50 psi (about 140-350 kPa) a 55% solids aqueous IAMS emulsion, having a viscosity of 355 cps (0.355 Pa.s), was supplied to the nozzle. As a result, the paper web was coated with adhesive droplets that formed islands ranging from 0.02 to 0.13 mm in diameter and about 0.2-0.05 mm in thickness. Higher air velocities or higher droplet velocities will cause the droplet to flatten out more when it strikes the paper. A lower viscosity adhesive will also cause the droplet to flatten. By increasing the viscosity of the adhesive and reducing the velocity of the droplet as it strikes the paper, the droplet can assume a nearly spherical shape on top of the paper. All will be more or less hemispherical, due to surface tension, but the radius of the droplet will vary. Adhesion of the coating, measured in accordance with the previously described test, was 23-28 g/cm width.

EXAMPLES 81 and 82

Using the same spray unit and coating conditions as in Example 80, a 61% solids aqueous emulsion of a 1:1.2 IAMS:adhesive microspheres of the type described in U.S. Pat. No. 3,691,140, having a viscosity of 158 cps (0.158 Pa.s) was sprayed onto the bond paper web, the distance between the spray unit and the web being fixed at 20 cm and 30 cm. Results are tabulated below:

| | Examples | |
|-----------------------------|-----------|-----------|
| | 81 | 82 |
| Spray unit-web distance, cm | 20 | 30 |
| Adhesion, g/cm | 37 | 15 |
| Island thickness, mm | 0.02-0.05 | 0.02-0.05 |
| Total spray diameter, cm | 4-8 | 6-10 |

-continued

| | Examples | |
|--------------------------|----------|------|
| | 81 | 82 |
| Overall coverage, % | | |
| Average Coverage, % | 65 | 41 |
| Average Adhesion, (g/cm) | 46.1 | 18.5 |
| Center of Pattern | | |
| Coverage, % | 74 | 45 |
| Adhesion, g/cm | 58.3 | 23.2 |
| Edge of Pattern | | |
| Coverage, % | 5-9 | 5-9 |
| Adhesion, g/cm | 2-4 | 2-4 |

The present invention is also applicable to the preparation of unique products for which there has existed a long-felt need. It is widely recognized, for example, that the paper used for disposable towels, tissues, and napkins are light weight and have very little internal strength. It is also recognized that such products have a distressing tendency to slide from the place they are designated to protect, often at the most inopportune moment. If a conventional coating of pressure-sensitive adhesive could be applied, it would serve to hold products of this type in position. It is, however, impractical or impossible to apply a conventional layer of pressure-sensitive adhesive by roll coating or rotogravure coating without tending to pick the paper apart during the coating operation. In addition, the adhesive properties of the conventional pressure-sensitive adhesive coating are sufficiently strong that the adhesive-coated paper would tend to delaminate on removal, leaving the user with a filmy paper product bonded to his clothing by a tenaciously bonded adhesive.

The present invention, which teaches a method of non-contact spray coating to achieve a discontinuous coating, overcomes the problems just described. This coating method will not drive the adhesive deep into the paper substrate and can be used on rough or embossed surfaces. Using a DeVilbiss spray gun (Model AGB 544 with a #110 air cap and an AV 1115FX-S

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nozzle, an acrylate emulsion adhesive having a solids content of 52% and a viscosity of 0.179 Pa.s was sprayed on the exposed edges of shingled stacks of single-ply yellow embossed napkins, tissues, and single-ply paper toweling. Each of the resultant products had an adhesive coating on the exposed portions in which the droplet diameter was 0.02–2.5 mm and the thickness was 0.02–0.06 mm. When placed on a wide variety of fabrics, each product remained in fixed position but could be readily removed without delamination. Individual sheets of the paper products could be protected by arranging them in pad format, rolling the shingled sheets into a roll, applying a cover sheet over the adhesive, folding each sheet so that it covered its own adhesive, folding the last sheet of paper in the stack back over its adhesive, etc.

It has also been found that tacky elastomeric microspheres (e.g., of the type described in U.S. Pat. No. 3,857,731) can also be included in the adhesive dispersions applied by the spray techniques described hereinabove, the microspheres becoming bonded to the backing by the dispersed adhesive.

In view of the foregoing applications for the invention, it is reasonable to use the same spray technique to coat conformable paper, plastic film, or aluminum foil substrates.

What is claimed is:

1. A method of making a removable and repositionable adhesive sheet product comprising spraying onto a sheet backing material a solution or dispersion of a normally tacky and pressure-sensitive adhesive in a liquid carrier and thereafter evaporating the liquid carrier, leaving a non-repetitive discontinuous pattern of spaced islands of adhesive, the pressure-sensitive adhesive being sufficiently adherent that, if sheet material having a continuous coating of said adhesive is applied to newsprint, it cannot be peeled away at normal removal rates without tearing or delaminating said newsprint, the adhesive islands being on the order of 0.01 to 0.15 millimeter thick, having at least one other dimension no greater than 0.02–1.5 millimeters, and occupying from about 10–85% of the area over which adhesive is applied, so as to achieve an adhesion to polyester film on the order of 8–80 grams per centimeter width, whereby said adhesive product can be adhered to newsprint, allowed to remain in contact therewith for two weeks at room temperature and then removed without visibly damaging the newsprint.

2. A method of making a removable and repositionable adhesive sheet product comprising spraying onto a sheet backing material a solution or dispersion of a normally tacky and pressure-sensitive adhesive in a liquid carrier and thereafter evaporating the liquid carrier, leaving a non-repetitive discontinuous pattern of spaced islands of adhesive, the pressure-sensitive adhesive being sufficiently adherent that, if sheet material having a continuous coating of said adhesive is applied to newsprint, it cannot be peeled away at normal removal rates without tearing or delaminating said newsprint, the adhesive islands being on the order of 0.01 to 0.15 millimeter thick, having at least one other dimension no greater than 0.02–1.5 millimeters, and occupying from about 10–85% of the area over which adhesive is applied, so as to achieve an adhesion to polyester film on the order of 8–80 grams per centimeter width, whereby said adhesive product can be adhered to newsprint, allowed to remain in contact therewith for two weeks at room temperature and then removed without

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visibly damaging the newsprint and; wherein the backing material is an elongate web and the solution or dispersion of adhesive is applied in a strip extending along the machine direction of the web.

3. A method of making a removable and repositionable adhesive sheet product comprising spraying onto a sheet backing material a solution or dispersion of a normally tacky and pressure-sensitive adhesive in a liquid carrier and thereafter evaporating the liquid carrier, leaving a non-repetitive discontinuous pattern of spaced islands of adhesive, the pressure-sensitive adhesive is sufficiently adherent that, if sheet material having a continuous coating of said adhesive is applied to newsprint, it cannot be peeled away at normal removal rates without tearing or delaminating said newsprint, the adhesive islands being on the order of 0.01 to 0.15 millimeter thick, having at least one other dimension no greater than 0.02–1.5 millimeters, and occupying from about 10–85% of the area over which adhesive is applied, so as to achieve an adhesion to polyester film on the order of 8–80 grams per square centimeter width, whereby said adhesive product can be adhered to newsprint, allowed to remain in contact therewith for two weeks at room temperature and then removed without visibly damaging the newsprint; wherein the strip of adhesive has a high population density of adhesive islands in one longitudinally extending area and a gradually decreasing population density toward at least one side of the strip.

4. A method of making a removable and repositionable adhesive sheet product comprising spraying onto a sheet backing material a solution or dispersion of a normally tacky and pressure-sensitive adhesive in a liquid carrier and thereafter evaporating the liquid carrier, leaving a non-repetitive discontinuous pattern of spaced islands of adhesive, the pressure-sensitive adhesive is sufficiently adherent that, if sheet material having a continuous coating of said adhesive is applied to newsprint, it cannot be peeled away at normal removal rates without tearing or delaminating said newsprint, the adhesive islands being on the order of 0.01 to 0.15 millimeter thick, having at least one other dimension no greater than 0.02–1.5 millimeters, and occupying from about 10–85% of the area over which adhesive is applied, so as to achieve an adhesion to polyester film on the order of 8–80 grams per square centimeter width, whereby said adhesive product can be adhered to newsprint, allowed to remain in contact therewith for two weeks at room temperature and then removed without visibly damaging the newsprint; wherein the strip of said adhesive has a high population density of adhesive islands in the central longitudinally extending area and a gradually decreasing population density toward both edges of the strip.

5. A method of making a removable and repositionable adhesive sheet product comprising spraying onto a sheet backing material a solution or dispersion of a normally tacky and pressure-sensitive adhesive in a liquid carrier and thereafter evaporating the liquid carrier, leaving a non-repetitive discontinuous pattern of spaced islands of adhesive, the pressure-sensitive adhesive being sufficiently adherent that, if sheet material having a continuous coating of said adhesive is applied to newsprint, it can not be peeled away at normal removal rates without tearing or delaminating said newsprint, the adhesive islands being on the order of 0.01 to 0.15 millimeter thick, having at least one other dimension no greater than 0.02–1.5 millimeters, and occupy-



US005378536A

United States Patent [19]

Miller et al.

[11] Patent Number: **5,378,536**[45] Date of Patent: **Jan. 3, 1995**[54] **REPOSITIONABLE ADHESIVE TAPE**[75] Inventors: **John A. Miller, Woodbury; George J. Clements, Afton, both of Minn.**[73] Assignee: **Minnesota Mining and Manufacturing Company, St. Paul, Minn.**[21] Appl. No.: **874,717**[22] Filed: **Apr. 27, 1992****Related U.S. Application Data**

[62] Division of Ser. No. 681,655, Apr. 8, 1991.

[51] Int. Cl.⁶ **C09J 7/02**[52] U.S. Cl. **428/355; 604/389; 604/390**[58] Field of Search **604/389, 390; 428/343, 428/355**[56] **References Cited****U.S. PATENT DOCUMENTS**

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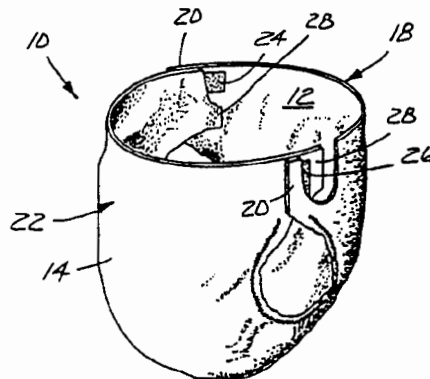
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Primary Examiner—Jenna L. Davis**Attorney, Agent, or Firm—Gary L. Griswold; Walter N. Kirm; William J. Bond**[57] **ABSTRACT**

An adhesive of certain elastomeric block copolymers and tackifying materials can be hot-melt coated onto a flexible backing to provide an adhesive tape, two pieces of which can bond to each other to have excellent resistance to shear forces but can be easily peeled apart, even after prolonged periods of time. The adhesive can be low-tack or tack-free. When the novel adhesive is tacky, it can bind sheets into a note pad from which individual sheets can be removed, temporarily adhered to paper and other substrates, and later cleanly removed, even after prolonged contact.

5 Claims, 1 Drawing Sheet

U.S. Patent

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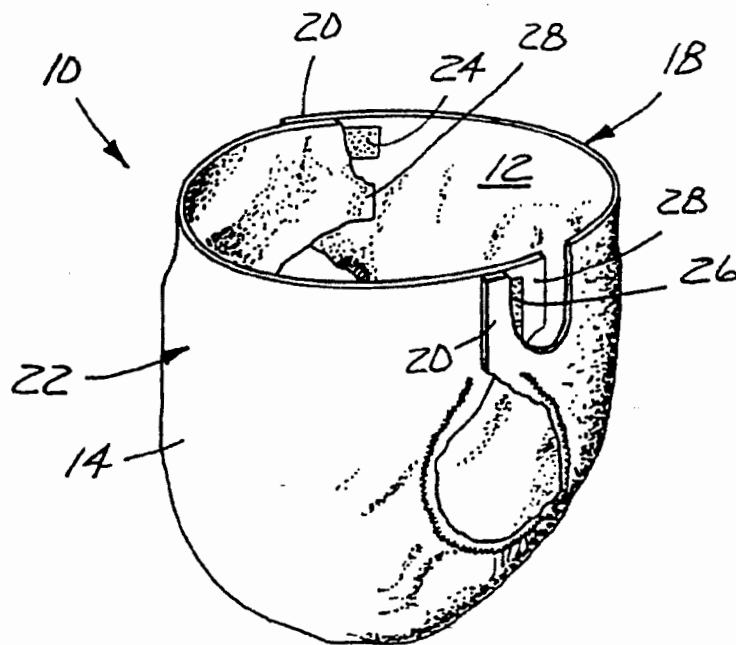


Fig. 1

REPOSITIONABLE ADHESIVE TAPE

This is a division of application Ser. No. 07/681,655 filed Apr. 8, 1991, pending.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is concerned with low-tack and tack-free adhesives that substantially do not experience adhesion build-up and so provide tapes that are repositionable, even after being adhered to a substrate for prolonged periods of time. Of special interest are low-tack pressure-sensitive adhesive note pads and adhesive diaper closures.

2. Description of the Related Art

POST-IT™ note pads have become virtually indispensable in the office, each sheet bearing a stripe of pressure-sensitive adhesive that is sufficiently tacky to adhere to paper and other substrates but does not show a buildup of adhesion. The sheets can be cleanly removed and reapplied a number of times without loss of tackiness. These attributes are realized due to the use of tacky microspheres coated onto the paper substrate, as disclosed in U.S. Pat. No. 3,691,140 (Silver). The same low-tack pressure-sensitive adhesive has been used for a number of other purposes, e.g. as a coating for a bulletin board or for posting ordinary pieces of paper.

The widespread success of the POST-IT™ note pads and the relatively high cost of the adhesive have resulted in efforts to produce a pressure-sensitive adhesive of a more simple, and hence more economical, composition that would provide the same attributes. However, it is believed that every known pressure-sensitive adhesive has been deficient in some important respect, e.g., being too aggressively tacky or lacking the desired initial holding power or being subject to a gradual buildup in adhesion.

An adhesive that is said to afford similar properties as that used in POST-IT™ note pads is the subject of U.S. Pat. No. 4,684,685 (Shuman et al.). Shuman et al.'s preferred adhesive includes a natural rubber latex and a tackifier which is an anionic aqueous dispersion of hydrogenated rosin or rosin esters. After coating the dispersion onto a substrate such as a sheet of paper, the dried coating allegedly has enough tack to adhere to solid contact surfaces by manually pressing the coated substrate to that surface. The Shuman patent says that the user can then "reapply the coated substrate as many as eight to ten additional times to the same or another free solid surface."

Although there have been attempts at providing alternative adhesive formulations which provide properties suitable for use as a repositionable adhesive, such as for repositionable note pads, there is still great interest in the discovery of yet more alternatives.

Of additional interest for repositionable low-tack adhesives, and otherwise, are adhesives which adhere to themselves yet are subsequently removable and re-adherable. Adhesives with these properties may or may not have repositionable tape or note pad properties. Advantageously, for certain applications these self-adhering adhesives will be relatively non-tacky or have no tack so that they exhibit adhesiveness to little else other than itself. Examples of such adhesives are discussed in U.K. Pat. No. GB 2,116,253B (Clerici et al.) and U.S. Pat. No. 4,522,874 (Pommez).

Clerici et al. releasably joins two objects using two pieces of "adhesive" tape that can be repeatedly engaged and disengaged. They state that this requires each of (a) the cohesive strength of the carriers, (b) anchoring of the adhesive layers to the carriers, and (c) the cohesive strength of the adhesive layers to be stronger than the force required to separate two engaged tapes. The Clerici et al. adhesive can be coated from "an elastomer for example natural rubber dissolved in a solvent such as heptane in the proportions of 15% natural rubber and 55% of heptane, by weight" (sentence bridging pages 8 and 9). Also useful is "a mixture of elastomeric materials, consisting for example of natural rubber and elastomers of a synthetic nature, such as butadiene-styrene rubber" (page 4, lines 17-24). The Clerici et al. "adhesive" is just rubber or a mixture of natural and synthetic rubber which is attached to an e.g., cloth backing.

Pommez illustrates a three-layer disposable diaper, the outer layer of which is "a porous paper-like substrate having one surface thereof coated with a selective adhesive which adheres only to itself" (col. 2, lines 38-41). Referring to FIG. 2: "Ears, or projections 54, of the back portion of the diaper, are also impregnated with the adhesive of the invention from inside, which enables its selective adhesion in any position on the outer surface, also impregnated, of the front portion 56, of the diaper. The qualities of the invention's adhesive enable the fastening and refastening of ear 54 until a perfect fit on the wearer's body obtained, or permits the diaper to be removed and used again later" (col. 4, lines 1-11). "The adhesive is comprised of an aqueous ammoniacal emulsion having about 60 percent solids and about 0.003 percent ammonia. The solids are about 85 parts by weight poly-cis-isoprene and about 15 parts by weight vinyl acetate and n-butyl acrylate" (col. 2, lines 41-45).

This emulsion of Pommez serves as an adhesive and as the means by which the outer shell (paper) is made water impermeable. There is no indication that this emulsion would be suitable for use in a tape or on a diaper which is not a porous paper substrate, e.g. a polyolefin backing which would severely limit the applicability of this self-adhering adhesive. Further use of a solvent based system is hampered by the need to subsequently remove and properly dispose of the solvent. This problem is particularly acute where the solvent is a volatile organic, as in Clerici et al.

The present invention has as a general object to solve or substantially alleviate the above noted problems in the art.

Another object of the invention is to provide an adhesive composition that is self-adhering.

A more specific object is to provide a self-adhering adhesive that can be subsequently removed and reapplied to itself.

A more specific object is to provide a self-adhering adhesive which is suitable for use as a repositionable diaper closure.

Another more specific object is to provide a self-adhering adhesive that has low or no adhesive buildup to itself.

Another object is to provide a repositionable adhesive.

A more specific object is to provide a repositionable adhesive which is adhesive to itself.

A further object of the present invention is to provide a method for applying these adhesives without the use of a solvent.

Further advantages and features of the invention, as well as the scope, nature and utilization of the invention will become apparent to those skilled in the art from the following description of the preferred embodiments of the invention.

SUMMARY OF THE INVENTION

The invention provides a low-tack or tack-free adhesive that can be coated onto a backing, generally flexible, to provide an adhesive tape, two pieces of which can bond to each other with excellent resistance to shear forces while still being easily peeled apart, even after prolonged periods of time. When the novel adhesive composition is low-tack, it is a pressure-sensitive adhesive and can have the attributes of the adhesives of the Silver patent, while being more economical to manufacture because it is hot-melt coatable and does not require tiny balls of a stiff pressure-sensitive adhesive or cause the environmental problems of solvent coating methods. Briefly, the novel adhesive comprises a composition of by weight:

from 20 to 80 parts of at least one elastomeric block copolymer selected from styrene/butadiene, styrene/isoprene, and styrene/ethylene-butylene block copolymers, and correspondingly from 80 to 20 parts of tackifying material selected from tackifier resins or blends and blends of tackifier resin with liquid plasticizer oil, which adhesive can be hot-melt coated without the use of solvents and has a composite midblock glass transition temperature (CMTg) from 225 Kelvin to 240 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers and a CMTg from 215 Kelvin to 235 Kelvin when the adhesive is based on styrene/butadiene block copolymer. The CMTg can be calculated using the Fox Equation from the measured Tg of the midblock of the elastomeric block copolymer and the measured Tg of each tackifying resin and liquid plasticizer oil. The Tg for each component is measured using a differential scanning calorimeter such as a DSC-7, manufactured by Perkin-Elmer. The Tg is measured on the second heating run using a scan rate of 20 degrees Centigrade per minute. The first heating run is made up to well above the softening point of the test material. The sample is subsequently quenched to well below the of the material. Antioxidants added to the adhesive are not figured into the calculation of the CMTg.

$$\text{Fox Equation } \frac{\sum_i W_i}{\text{CMTg}} = \sum_i \frac{W_i}{T_{gi}}$$

where W_i is the weight fraction of component i and T_{gi} is the glass transition temperature of component i . Only the midblock portion of the block copolymer is included in the calculation of the CMTg. For a styrene/isoprene block copolymer, the midblock portion is the polyisoprene portion of the molecule.

The tackifier resin or blend, or blend of tackifier resin(s) and liquid plasticizer oil(s) of the novel adhesive can be any of

- solid tackifier resin(s),
- liquid tackifier resin(s),

blend of a solid tackifier resin(s) and liquid tackifier resin(s),

a blend of a solid tackifier resin(s) and liquid plasticizer oil(s), and

a blend of solid tackifier resin(s), liquid tackifier resin(s), and liquid plasticizer oil(s).

The blends are preferred, because they give a formulator more control over the rheological properties of the adhesive than does the use of a single tackifier resin. For example, when the proportion of elastomeric block copolymer is near the high end (i.e., 55-80 parts) and the CMTg is near the high end (i.e., within 10 Kelvin) of the aforementioned ranges, the novel adhesive tends to have high resistance to shear forces and to be low-tack or tack-free. This type of adhesive will be best suited for use as a self-adhering adhesive. Its low, or no, tack makes it have little or no adhesion to other substrates while its high resistance to shear when attached to itself makes it ideal for a reusable adhesive closure system.

On the other hand, the novel adhesive can be somewhat tacky when the proportion of elastomeric block copolymer is near the low end (i.e., 20-45 parts) and the CMTg is near the high end of those ranges. These adhesives are generally usable as repositionable adhesive tapes, however, they will have a tendency to buildup adhesion over extended periods of time. These adhesives however will still be self-adhering and show the characteristics discussed above.

The least buildup of adhesion to other substrates is realized when both the proportion of elastomeric block copolymer and the CMTg are relatively low. These adhesives are the best suited for use as a repositionable tape on note pads, such as is used in a Post-it™ pad. These tapes, however, will still display self adhesion properties, although generally with lower shear resistance.

Overall, the lower buildup of adhesion to other substrates seems to be primarily related to CMTg while the tendency to build up adhesion to itself seems to be primarily a function of percent polymer concentration. However, these observations are merely generally noted trends, and suitable adhesives for, e.g., self-adhering tape applications or repositionable tapes can be found outside the most likely areas to find such tapes within the invention composition.

In addition to the foregoing components, the adhesive of the invention can incorporate small amounts of other materials commonly used in pressure-sensitive adhesives, e.g. antioxidants such as hindered phenols and hydroquinones, heat stabilizers such as zinc carbamates, ultraviolet stabilizers, fillers, and pigments. Such additional materials can be disregarded in the CMTg calculation.

The adhesive of the invention can be economically converted to tapes by being coated onto backings at high speeds without the use of solvents, or can be coated from solution when that is more convenient. Depending on the backing, the backings can be surface treated to promote adhesion of the adhesive thereto. The resulting tapes can be marketed in strips or in wide sheets and usually have flexible backings for ease of storage, handling, and application. For example, of the novel adhesive can be coated onto paper which is then cut and stacked to form a tablet or note pad of repositionable sheets like the aforementioned POST-IT™ note pads. For such use, the adhesive is preferably somewhat tacky so that sheets of a note pad will adhere

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temporarily to paper and other substrates from which they can later be cleanly removed.

For uses requiring the adhesive to be somewhat tacky, such as for a repositionable note pad, the CMTg can be as low as 220 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers which comprise up to 45% by weight of the adhesive.

Whether or not the novel adhesive is low-tack or tack-free, pieces of tape bearing the adhesive have a remarkable ability to form bonds to each other that have excellent resistance to shear forces. In tests, even after four months at ordinary room temperatures, two tapes bearing the novel adhesive separate cleanly between their adhesive layers. The same tapes also separate cleanly after two hours at 37° C. However, low tack adhesives with properties best suited for use as a repositionable adhesive have a tendency to block slightly at above ambient temperatures (e.g., at 37° C.). Therefore, these adhesives would not be as desirable for self-adhering adhesive closures used in close contact with a heated body, such as in a diaper closure system.

In any event, the ability of certain inventive compositions to separate cleanly after 2 hours at 37° C. would make these inventive adhesives well suited for reclosable apparel closures that are used in close proximity to the wearer. Examples of uses for such closure systems include diapers, incontinence devices, surgical gowns, hats or booties, clean room garments, ankle bands, wrist bands or the like. When used, as in reclosable apparel closures, the adhesive can be directly applied to the article or applied as a tape where the side which is permanently attached to the article can have a suitable conventional adhesive. The adhesive would generally be applied as patches on each side of a closure point, e.g., on opposing faces of at least two closure elements that mate to complete the closure. When the two closure elements of the article are brought into contact the adhesive patches will come into contact yielding a re-sealable closure. The patches can be of a size and arrangement such that they will contact each other over a number of overlapping positions of the closure elements to form an adjustable closure.

For example, the novel adhesive can be used to provide a reclosable disposable diaper by applying a patch of the adhesive to the inner face of each of the corners at the back of a disposable diaper and also to the outer shell where the front of the diaper can be overlapped by the corners when the diaper is wrapped around the waist of a person. The face-to-face contact between those adhesive patches holds the diaper securely in place, but these patches can be easily peeled apart, either to remove or to refasten the diaper.

Where a closure system is used at ambient conditions generally any adhesive composition of the invention can be used with suitable adjustment of the size, shape, and location of the adhesive patches to account for slight variations in the strength of the adhesive bonding strength.

The novel adhesive also can be used to permit labels and masking tapes to be cleanly removed from substrates to which they may be applied. Other useful tape articles of the invention that have flexible backings include reclosable mailing envelopes, resealable bags, adhesive-backed sandpaper and sanding disks, and decals. The novel adhesive also can be marketed in a spray can from which layers can be applied for uses such as temporarily mounting posters or photographs.

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DETAILED DISCLOSURE

Elastomeric block copolymers that are useful in the adhesive of the invention can have any of the common configurations of the block structure including linear diblock and triblock, radial, star, and tapered geometries. Useful elastomers include styrene/isoprene block copolymers such as "Kraton" 1107 and "Kraton" 1111, available from Shell Chemical Co.; "Enichem" SOL T 190, available from Enichem U.S.A.; "Quintac" 3421, "Quintac" 3430 and "Quintac" 3530, available from Nippon-Zeon; Finaprene 424, available from Fina Chemical Co.; styrene/butadiene block copolymers such as "Kraton" 1101 and 1102; "Stereon" 840A, available from Firestone Synthetic Latex and Rubber Co., and "Enichem" Sol T 1205 and Sol T 161 C; and styrene/ethylene-butylene block copolymers such as "Kraton" 1657 and 1650.

Tackifier resins that are useful in the novel adhesives include those aliphatic hydrocarbon resins made from the polymerization of a feed stream consisting mainly of unsaturated species containing four to six carbon atoms, such as "Wingtack" 10, "Wingtack Plus", and "Wingtack" 95, available from the Goodyear Tire and Rubber Co.; "Escorez" 1310, available from Exxon Chemical Co., and "Hercotac" RT-95, available from Hercules, Inc.; rosin esters and rosin acids such as "Hercoflex" 400, "Hercoflex" 500, "Foral" 85, "Regalite" 355, and "Permalyn" 305, all available from Hercules, Inc.; mixed aliphatic/aromatic liquid tackifiers such as "Escorez" 2520 available from Exxon Chemical Co.; and polyterpene tackifiers such as "Zonarez" A-25 and "Zonarez" A-100, available from Arizona Chemical Co. and "Piccolyte" HM-85, HM-105, and S-115 available from Hercules, Inc. Also useful are the general class of hydrogenated tackifying resins, including ECR-327, "Escorez" 5380, "Escorez" 5300, "Escorez" 5320, and "Escorez" 5340, all available from Exxon Chemical Co.; "Regalrez" 1018, "Regalrez" 1065, "Regalrez" 1078, "Regalrez" 1094, and "Regalrez" 1126, all available from Hercules Inc.; and "Arkon" P-90, "Arkon" P-100, "Arkon" M-90, and "Arkon" M-100, available from Arakawa Chemical Co.; hydrogenated polyterpene resins such as "Nirez" K-85, "Nirez" K-105, and "Nirez" K-110, available from Reichhold Chemicals, Inc.; and hydrogenated aliphatic and aliphatic/aromatic resins such as ECR-142H and ECR-143H, available from Exxon Chemical Co. Preferred tackifying resins include the aliphatic hydrocarbon resins, the hydrogenated resins, and the polyterpene resins. Especially preferred are the aliphatic hydrocarbon resins.

The liquid plasticizer oils suitable for use in the adhesive of the invention include naphthenic oils such as "Shellflex" 371, available from Shell Chemical Co., paraffinic oils, aromatic oils, and mineral oils such as "Kaydol" oil, available from Witco Chemical Corp. Preferred liquid plasticizers include naphthenic oil and mineral oil.

THE DRAWING

The invention may be more easily understood in reference to the following drawing, in which:

FIG. 1 is a schematic view of a disposable diaper as it would appear while being worn by a person.

The disposable diaper shown in FIG. 1 is a conventional three layer composite including a liquid-permeable user-contacting topsheet 12, a liquid-impervious outer shell (backsheet) 14, and an absorbent layer there-

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between (not shown). At the back 18 of the diaper are corners 20 that overlap the front of the diaper 22 at corners 28 when the diaper is worn as shown. On the topsheet side of each corner 20 is placed a patch of the inventive adhesive 24. On the outer shell 14 at the front 22 of the diaper are two patches 26 of the inventive adhesive. The patches are placed on the diaper such that they will come into contact when the diaper is worn as shown.

The overlapping portions of the adhesive patches should provide a force to peel generally from 2 to 12N, preferably from 5 to 7N. To provide this peel force resistance and still provide for adjustability, the adhesive patches are placed as is shown in FIG. 1. Each patch would be preferably from 3 to 6 cm in length and from 1.5 to 3 cm in width. The lengthwise directions of the patches are preferably orthogonal to each other. This orientation will provide the greatest degree of adjustability for the preferred patches. Where the patches are so oriented and overlap over an entire width portion, the area of contact will be from 1.75 cm² to 9 cm² for rectilinear shaped patches. Generally this degree of overlap provides sufficient peel resistance for use as a diaper closure system while avoiding excessive or wasteful use of the adhesive.

TESTING

Some tapes bearing the adhesive of the invention were subjected to one or more of the following tests:

Probe Tack Value

This is run according to ASTM D-2979 except using a Polyken Probe Tack tester with a polypropylene probe at a 1 cm/second probe speed, a 1 second dwell time, and a 100 gram/cm² load.

90° Peel Value

This is run according to PSTC-5 using a polyethylene substrate to which the test tape was applied using a 2-kg hard rubber roller, one pass in each direction at 30 cm/min. An adhesive which has a 90° Peel Value of from 2 to 8N/25 mm should be useful for making note pads of repositionable sheets like POST-ITTM note pads, because such adhesive-bearing sheets should adhere well to paper and other substrates while being removable without picking fibers, even after prolonged periods of time. When the 90° Peel Value is from 0 to 2N/25 mm, the adhesive would be most useful in the above-described adhesive-to-adhesive diaper closure as these are the least likely to adhere to ordinary packaging materials or to the non-adhesive surfaces of the diaper and hence will not require the use of a protective tape. However, protective tapes can be avoided with even higher peel values. For example, repositionable adhesive formulations may adhere to the diaper parts, however, this may be used to advantage in keeping the diaper folded or at worst be ignored as not affecting tape performance.

180° Peel Value

This is run according to ASTM D-1000 except that the adhesive tape is applied to various substrates using a 2-kg hard rubber roller, one pass in each direction at 30 cm/min, and testing was carried out after less than 20 minutes dwell at ordinary room temperature. The peel rate is 30 cm/min when the substrate is paper and 225 cm/min when the substrate is metal or plastic.

Tapes are also tested after two weeks of accelerated aging at 120° F. (49° C.) and then allowed to cool to room temperature for testing.

180° Dynamic Shear Value

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This value was determined using ASTM Test Method D3528-76 at a crosshead speed of 10 inches (25 cm) per minute.

T-Peel Value

This value was determined using ASTM Test Method D1876-72 at a crosshead speed of 10 inches (25 cm) per minute.

Self-Adhesion Peel Value

With the adhesive layers of two pieces of the same adhesive tape face-to-face, a 2-kg hard rubber roller is applied, one pass in each direction at 30 cm/min. The resulting sandwich is tested for T-peel by ASTM D-1876 at 30 cm/min.

Shear Adhesion Value

A one-inch square (2.54 cm-square) area of a test tape is laid with its adhesive layer against an embossed polyethylene substrate that is used as the backsheet of LUV's brand disposable diapers manufactured by Procter and Gamble and is about 30 μm thick. To enhance the stiffness of the substrate, the polyethylene substrate is laminated to a pressure-sensitive adhesive tape, viz., Release Tape Y-9378 manufactured by 3M Co. On the side opposite the reinforcing tape, the test tape is rolled down onto the polyethylene substrate with a 2-kg hard rubber roller, one pass in each direction at 30 cm/min. The laminated substrate and the test tape are hung vertically in a 40° C. oven for 15 minutes and a 500-gram weight is promptly hung from the test tape. The time for the weight to drop at 40° C. is the Shear Adhesion Value.

The following examples, in which all parts are by weight, are given by way of illustration and are not intended to limit the scope of the invention in any way. Commercial materials used in the examples were:

| | | | MTg |
|-------------------------------------|---|--|-------|
| <u>ELASTOMERIC BLOCK COPOLYMERS</u> | | | |
| "Finaprene" 424 | Styrene/isoprene block copolymer | | 215 K |
| "Kraton" 1101 | Styrene/butadiene block copolymer | | 188 K |
| "Kraton" 1107 | Styrene/isoprene block copolymer | | 215 K |
| "Kraton" 1111 | Styrene/isoprene block copolymer | | 215 K |
| "Kraton" 1657 | Styrene/ethylene-butylene block copolymer | | 215 K |
| "Quintac" 3430 | Styrene/isoprene block copolymer | | 215 K |
| | | | Tg |
| <u>SOLID TACKIFIER RESINS</u> | | | |
| "Arkon" P-90 | Hydrogenated hydrocarbon | | 309 K |
| "Escorez" 1310 | C5 aliphatic | | 314 K |
| "Escorez" 5300 | Hydrogenated hydrocarbon | | 323 K |
| "Foral" 85 | Rosin ester | | 313 K |
| "Piccolyte" HM-105 | Styrenated terpene | | 327 K |
| "Regalite" 355 | Hydrogenated rosin acid | | 318 K |
| "Regalrez" 1094 | Hydrogenated hydrocarbon | | 310 K |
| "Wingtack" 95 | C5 aliphatic | | 323 K |
| "Wingtack Plus" | C5 aliphatic | | 315 K |
| "Zonarez" A-100 | Alpha-pinene | | 328 K |
| <u>LIQUID TACKIFIER RESINS</u> | | | |
| ECR-143H | Hydrogenated hydrocarbon | | 247 K |
| "Escorez" 2520 | Aromatic/aliphatic | | 253 K |
| "Hercoflex" 500 | Rosin ester | | 238 K |
| "Wingtack" 10 | C5 aliphatic | | 245 K |
| "Zonarez" A-25 | Alpha-pinene | | 251 K |
| <u>LIQUID PLASTICIZER OILS</u> | | | |
| "Kaydol" Oil | Mineral oil | | 199 K |
| "Shellflex" 371 | Naphthenic oil | | 209 K |
| <u>ANTIOXIDANTS</u> | | | |
| "Irganox" 1076 | Hindered Phenol (available from Ciba-Geigy) | | |
| "Irganox" 1010 | Hindered Phenol | | |

EXAMPLES 1-18

Eighteen adhesive compositions were prepared by dissolving in toluene the components of the formulations given in Table I. One part of "Irganox" 1076 was added to each adhesive composition. Each adhesive solution was 65% by weight of solvent. Tape samples were prepared by coating the adhesive solutions onto a matte-finish cast-polypropylene backing having a thickness of 100 μm . The coating weight of the adhesive after drying at 60° C. for 5 minutes was about 3.5 mg/cm².

Results of testing the tapes of Examples 1-18 are reported in Table II.

TABLE I

| (Compositions for Examples 1-9 in Parts) | | | | | | | | | |
|--|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| | Example | | | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| "Finaprene" 424 | 60 | | | | | | | | |
| "Kraton" 1107 | | 75 | 50 | 65 | 40 | 80 | | | |
| "Kraton" 1111 | | | | | | | 50 | 45 | 80 |
| "Escorez" 2520 | | 23 | 47 | 19 | | | | | |
| "Kaydol" Oil | | | | | | 31 | 26 | | |
| "Shellflex" 371 | | | | | 43 | 7 | | | |
| "Zonarez" A-25 | 32 | | | | | | | | 16 |
| "Arkon" P-90 | | 2 | 3 | 16 | | | | | |
| "Escorez" 1310 | 8 | | | | | | | | |
| "Escorez" 5300 | | | | | | | 19 | 29 | |
| "Wingtack Plus" | | | | | 17 | 13 | | | |
| "Zonarez" A-100 | | | | | | | | | 4 |
| Composite Midblock Tg (Kelvin) | 235 | 225 | 235 | 235 | 225 | 225 | 225 | 235 | 225 |

| (Compositions for Examples 10-18 in Parts) | | | | | | | | | |
|--|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| | Example | | | | | | | | |
| | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| "Kraton" 1101 | | | | | | 20 | 50 | | |
| "Kraton" 1111 | 50 | 70 | | | | | | | |
| "Kraton" 1657 | | | | | | | | 70 | 40 |
| "Quintac" 3430 | | | 75 | 40 | 60 | | | | |
| ECR-143H | | | | | | | | 29 | 58 |
| "Shellflex" 371 | | | | | | 57 | 23 | | |
| "Wingtack" 10 | | | 20 | 56 | 24 | | | | |
| "Zonarez" A-25 | 48 | 16 | | | | | | | |
| "Arkon" P-90 | | | | | | | | 1 | 2 |
| "Piccolyte" HM-105 | | | | | | 23 | 27 | | |
| "Regalrez" 1094 | | | 5 | 4 | 16 | | | | |
| "Zonarez" A-100 | 2 | 14 | | | | | | | |
| Composite Midblock Tg (Kelvin) | 235 | 235 | 225 | 235 | 235 | 225 | 225 | 225 | 235 |

TABLE II

| Ex-ample | Probe Tack (N) | 90 Peel Value (N/25 mm) | Shear Adhesion Value (minutes) | Self-Adhesion Peel Value (N/25 mm) |
|----------|----------------|-------------------------|--------------------------------|------------------------------------|
| 1 | 4.2 | 1.4 | 2 | 2.2 |
| 2 | 0.9 | 0.3 | <1 | 2.1 |
| 3 | 4.5 | 1.1 | 2 | 2.2 |
| 4 | 3.3 | 1.4 | 1 | 1.6 |
| 5 | 3.2 | 0.4 | 3 | 1.6 |
| 6 | 1.6 | 1.0 | 1 | 1.0 |
| 7 | 2.2 | 0.7 | 3 | 0.5 |
| 8 | 6.5 | 2.0 | 26 | 0.9 |
| 9 | 0.9 | 0.3 | 16 | 1.2 |
| 10 | 3.5 | 2.0 | 2 | 0.9 |
| 11 | 3.0 | 1.5 | 25 | 1.6 |
| 12 | 1.1 | 0.4 | 1 | 0.8 |
| 13 | 5.9 | 2.7 | 6 | 2.5 |
| 14 | 3.9 | 1.9 | 11 | 2.7 |
| 15 | 2.9 | 0.2 | <1 | 0.2 |
| 16 | 2.6 | 0.8 | <1 | 0.6 |
| 17 | 0.2 | 0.1 | <1 | 2.3 |
| 18 | 2.9 | 0.4 | 11 | 3.4 |

EXAMPLES 19-22

A series of adhesive compositions was made as reported in Table III, and each was dissolved in toluene to a total solids concentration of 25%, with 0.5% of "Irganox" 1010 added to stabilize the adhesive against aging. Each composition was then coated onto a 25 μm thick biaxially oriented poly(ethylene terephthalate) backing and dried to a dry coating weight of about 1.0 mg/cm². The blocks in the star block copolymer used in Examples 20-22 have a linear configuration, with the isoprene chain capped on each end with styrene chains and were prepared in accordance with the procedure outlined in U.S. Pat. No. 4,780,367, the substance of

which is incorporated herein by reference, using a divinylbenzene catalyst to yield a polymer with 16.8% styrene and the remainder predominately isoprene. Results of testing each of Examples 19-22 for 180° Peel Value are reported in Table IV.

TABLE III

| (Compositions for Examples 19-22) | | | | |
|--|------|------|------|-------|
| Material | 19 | 20 | 21 | 22 |
| "Kraton" 1107 | 80 | | | 17 |
| Star block polymer of styrene/isoprene | | 35 | 20 | 25.5 |
| "Wingtack Plus" | 17.4 | 0.3 | 1.7 | 0.3 |
| "Wingtack" 10 | 2.6 | 64.7 | 78.3 | 57.2 |
| CMTg | 230 | 235 | 240 | 232.5 |

TABLE IV

| (180° Peel Value in N/25 mm) | | | | |
|------------------------------|-----|-----|-----|-----|
| Substrate | 19 | 20 | 21 | 22 |
| Paper | 1.7 | 3.2 | 5.0 | 2.4 |
| After aging | 4.1 | 8.9 | 6.6 | 7.0 |

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TABLE IV-continued

| Substrate | (180° Peel Value in N/25 mm) | | | |
|-----------------|------------------------------|----|----|----|
| | 19 | 20 | 21 | 22 |
| Stainless Steel | 16 | 11 | 25 | 17 |
| After aging | 31 | 25 | 35 | 28 |
| BOPP | 19 | 13 | 24 | 20 |
| After aging | 18 | 19 | 26 | 20 |
| PET | 28 | 18 | 23 | 22 |
| After aging | 28 | 29 | 35 | 27 |

Paper = ordinary bond copypaper

BOPP = biaxially oriented polypropylene

PET = biaxially oriented poly(ethylene terephthalate)

The data reported in Table IV show that each of the adhesives of Examples 19-22 has low adhesion to paper and other substrates and has low adhesion build-up with time evidenced by low adhesion after accelerated aging for two weeks at 49° C. This demonstrates that the adhesive of any of Examples 19-22 should be a suitable substitute, in repositionable note pads, for the adhesive of the above-cited Silver patent, even though these are not preferred examples of such substitute adhesives.

EXAMPLE 23

A handsread of 50% solution in toluene of 70 parts of "Kraton" 1657 and 30 parts of "Res" D-2084 was pulled onto biaxially oriented poly(ethylene terephthalate) film having a thickness of 12.5 μ m. The dried coating weight was about 24 g/m². This adhesive had:

CMTg=238 Kelvin

180° Dynamic Shear Value to itself=588N/cm²

T-Peel Value=6.5N/25 mm

COMPARATIVE EXAMPLES A-G

A series of tapes were made in the same way as the tapes of Examples 1-18 except using adhesive compositions indicated in Table V. Some of the adhesive compositions were as taught in the prior art as follows:

| Comparative Example | Adhesive as Taught in |
|---------------------|--|
| F | Sample 10 of Example III in U.S. Pat. No. 3,954,692 (Downey) |
| G | Example 4 of U.S. Pat. No. 3,932,328 (Korpmann) |

TABLE V

(Compositions in Parts)

| | Comparative Example | | | | | | |
|----------------------|---------------------|-----|-----|-----|-----|-----|-----|
| | A | B | C | D | E | F | G |
| "Finaprene" 424 | 40 | | | | | | |
| "Kraton" 1107 | | 50 | | | | 100 | 100 |
| "Quintac" 3430 | | | 40 | 30 | 40 | | |
| "Wingtack" 10 | | | | 26 | 11 | | 40 |
| "Zonarez" A-25 | 22 | | | | | 20 | |
| "Kaydol" Oil | | | 6 | | | | |
| "Shellflex" 371 | | 8 | | | | | |
| "Wingtack" 95 | | | | | | 100 | 100 |
| "Escorrez" 1310 | 38 | | | | | | |
| "Regalite" 355 | | | 54 | | | | |
| "Regalrez" 1094 | | | | 44 | 49 | | |
| "Wingtack Plus" | | 42 | | | | | |
| Composite | 258 | 250 | 262 | 260 | 260 | 254 | 254 |
| Midblock Tg (Kelvin) | | | | | | | |

Testing of comparative examples A-G is reported in Table VI.

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TABLE VI

| Example | Probe Tack (N) | 90° Peel Value (g/25 mm) | Shear Adhesion Value (minutes) | Self-Adhesion Peel Value (N/25 mm) |
|---------|----------------|--------------------------|--------------------------------|------------------------------------|
| | | | | |
| A | 13 | 7.3 | >1000 | 15 |
| B | 10 | 4.6 | >1000 | 12 |
| C | 10 | 13.6 | >1000 | 12 |
| D | 9 | 9.3 | >1000 | 18 |
| E | 12 | 8.0 | >1000 | 17 |
| F | 11 | 4.9 | >1000 | 18 |
| G | 10 | 7.8 | >1000 | 16 |

As indicated in Tables II and VI, comparative Examples A through G exhibit tack, peel, shear and self-adhesion values that are substantially greater than Example 1 through 18 and are typical of conventional pressure-sensitive adhesives that are based on elastomeric block copolymers.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A resealable cohesive adhesive closure system comprising;

an article having at least one resealable cohesive adhesive closure,

the at least one adhesive closure comprising two opposing closure elements at separate locations on said article, said opposing closure elements capable of overlapping to form said at least one resealable article adhesive closure,

self-adhering adhesive on each of said at least two closure elements comprising by weight:

from 20 to 80 parts of at least one elastomeric block copolymer selected from the group consisting of styrene/butadiene, styrene/isoprene, and styrene/ethylene-butylene block copolymers, and

correspondingly from 80 to 20 parts of tackifying material selected from tackifier resin and a blend of tackifier resin and liquid plasticizer oil; which self-adhering adhesive has a composite midblock glass transition temperature (CMTg) from 225 Kelvin to 240 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers and a CMTg from 215 Kelvin to 235 Kelvin when the adhesive is based on styrene/butadiene block copolymer.

2. The resealable adhesive closure system of claim 1 wherein said self-adhering adhesive has a 90° Peel Value of 0 to 2N/25 mm.

3. The resealable adhesive closure system of claim 1 wherein the adhesive CMTg is from 230 Kelvin to 240 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers and a CMTg from 225 Kelvin to 235 Kelvin when the adhesive is based on styrene/butadiene block copolymer.

4. The resealable adhesive closure system of claim 1 wherein the adhesive on said opposing closure elements is in the form of an adhesive patch, and, when said closure elements overlap, the adhesive patches bond to each other to form said closure having a peel force bond of from 2 to 12N.

5. The resealable adhesive closure system of claim 4 wherein said adhesive patches are each 3 to 6 cm in length and from 1.5 to 3 cm in width, with the lengthwise direction of each adhesive patch being orthogonal to the lengthwise direction of the adhesive patch on the opposing closure element.

* * * * *



US005389438A

United States Patent [19][11] **Patent Number:** **5,389,438****Miller et al.**[45] **Date of Patent:** **Feb. 14, 1995**[54] **REPOSITIONABLE ADHESIVE TAPE**[75] **Inventors:** **John A. Miller; George J. Clements,**
both of St. Paul, Minn.[73] **Assignee:** **Minnesota Mining and**
Manufacturing Company, St. Paul,
Minn.[21] **Appl. No.:** **681,655**[22] **Filed:** **Apr. 8, 1991****Related U.S. Application Data**

[63] Continuation of Ser. No. 483,130, Feb. 22, 1990, abandoned.

[51] **Int. Cl.⁶** **C09J 7/02**[52] **U.S. Cl.** **428/355; 428/512;**
525/98; 525/99[58] **Field of Search** **428/355, 512; 525/95,**
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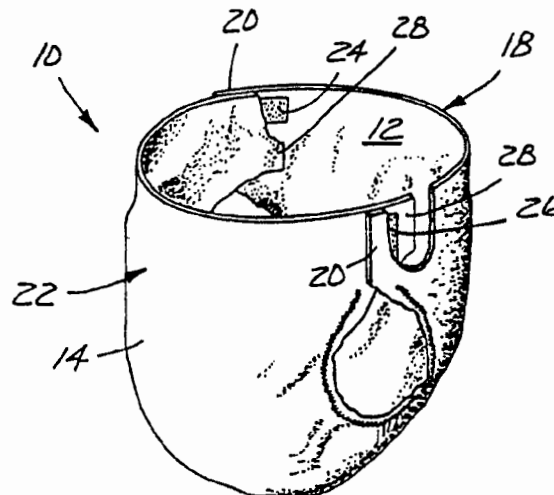
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Primary Examiner—Jenna L. Davis**Attorney, Agent, or Firm**—Gary L. Griswold; Walter N. Kirn; William J. Bond[57] **ABSTRACT**

An adhesive of certain elastomeric block copolymers and tackifying materials can be hot-melt coated onto a flexible backing to provide an adhesive tape, two pieces of which can bond to each other to have excellent resistance to shear forces but can be easily peeled apart, even after prolonged periods of time. The adhesive can be low-tack or tack-free. When the novel adhesive is tacky, it can bind sheets into a note pad from which individual sheets can be removed, temporarily adhered to paper and other substrates, and later cleanly removed, even after prolonged contact.

8 Claims, 1 Drawing Sheet

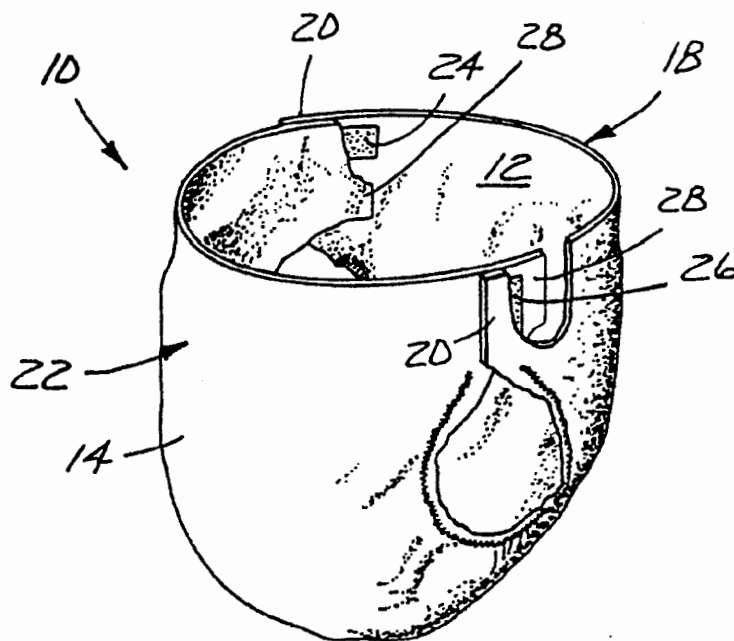


Fig. 1

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REPOSITIONABLE ADHESIVE TAPE

This is a continuation of application Ser. No. 07/483,130, filed Feb. 22, 1990, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is concerned with low-tack and tack-free adhesives that substantially do not experience adhesion build-up and so provide tapes that are repositionable, even after being adhered to a substrate for prolonged periods of time. Of special interest are low-tack pressure-sensitive adhesive note pads and adhesive diaper closures.

2. Description of the Related Art

POST-IT™ note pads have become virtually indispensable in the office, each sheet bearing a stripe of pressure-sensitive adhesive that is sufficiently tacky to adhere to paper and other substrates but does not show a buildup of adhesion. The sheets can be cleanly removed and reapplied a number of times without loss of tackiness. These attributes are realized due to the use of tacky microspheres coated onto the paper substrate, as disclosed in U.S. Pat. No. 3,691,140 (Silver). The same low-tack pressure-sensitive adhesive has been used for a number of other purposes, e.g. as a coating for a bulletin board or for posting ordinary pieces of paper.

The widespread success of the POST-IT™ note pads and the relatively high cost of the adhesive have resulted in efforts to produce a pressure-sensitive adhesive of a more simple, and hence more economical, composition that would provide the same attributes. However, it is believed that every known pressure-sensitive adhesive has been deficient in some important respect, e.g., being too aggressively tacky or lacking the desired initial holding power or being subject to a gradual buildup in adhesion.

An adhesive that is said to afford similar properties as that used in POST-IT™ note pads is the subject of U.S. Pat. No. 4,684,685 (Shuman et al.). Shuman et al.'s preferred adhesive includes a natural rubber latex and a tackifier which is an anionic aqueous dispersion of hydrogenated rosin or rosin esters. After coating the dispersion onto a substrate such as a sheet of paper, the dried coating allegedly has enough tack to adhere to solid contact surfaces by manually pressing the coated substrate to that surface. The Shuman patent says that the user can then "reapply the coated substrate as many as eight to ten additional times to the same or another free solid surface."

Although there have been attempts at providing alternative adhesive formulations which provide properties suitable for use as a repositionable adhesive, such as for repositionable note pads, there is still great interest in the discovery of yet more alternatives.

Of additional interest for repositionable low-tack adhesives, and otherwise, are adhesives which adhere to themselves yet are subsequently removable and re-adherable. Adhesives with these properties may or may not have repositionable tape or note pad properties. Advantageously, for certain applications these self-adhering adhesives will be relatively non-tacky or have no tack so that they exhibit adhesiveness to little else other than itself. Examples of such adhesives are discussed in U.K. Pat. No. GB 2,116,253B (Clerici et al.) and U.S. Pat. No. 4,522,874 (Pommez).

Clerici et al. releasably joins two objects using two pieces of "adhesive" tape that can be repeatedly engaged and disengaged. They state that this requires each of (a) the cohesive strength of the carriers, (b) the anchoring of the adhesive layers to the carriers, and (c) the cohesive strength of the adhesive layers to be stronger than the force required to separate two engaged tapes. The Clerici et al. adhesive can be coated from "an elastomer for example natural rubber dissolved in a solvent such as heptane in the proportions of 15% natural rubber and 55% of heptane, by weight" (sentence bridging pages 8 and 9). Also useful is "a mixture of elastomeric materials, consisting for example of natural rubber and elastomers of a synthetic nature, such as butadiene-styrene rubber" (page 4, lines 17-24). The Clerici et al. "adhesive" is just rubber or a mixture of natural and synthetic rubber which is attached to an, e.g., cloth backing.

Pommez illustrates a three-layer disposable diaper, the outer layer of which is "a porous paper-like substrate having one surface thereof coated with a selective adhesive which adheres only to itself" (col. 2, lines 38-41). Referring to FIG. 2: "Ears, or projections 54, of the back portion of the diaper, are also impregnated with the adhesive of the invention from inside, which enables its selective adhesion in any position on the outer surface, also impregnated, of the front portion 56, of the diaper. The qualities of the invention's adhesive enable the fastening and refastening of ear 54 until a perfect fit on the wearer's body is obtained, or permits the diaper to be removed and used again later" (col. 4, lines 1-11). "The adhesive is comprised of an aqueous ammoniacal emulsion having about 60 percent solids and about 0.003 percent ammonia. The solids are about 85 parts by weight poly-cis-isoprene and about 15 parts by weight vinyl acetate and n-butyl acrylate" (col. 2, lines 41-45).

This emulsion of Pommez serves as an adhesive and as the means by which the outer shell (paper) is made water impermeable. There is no indication that this emulsion would be suitable for use in a tape or on a diaper which is not a porous paper substrate, e.g. a polyolefin backing which would severely limit the applicability of this self-adhering adhesive. Further use of a solvent based system is hampered by the need to subsequently remove and properly dispose of the solvent. This problem is particularly acute where the solvent is a volatile organic, as in Clerici et al.

The present invention has as a general object to solve or substantially alleviate the above noted problems in the art.

Another object of the invention is to provide an adhesive composition that is self-adhering.

A more specific object is to provide a self-adhering adhesive that can be subsequently removed and reapplied to itself.

A more specific object is to provide a self-adhering adhesive which is suitable for use as a repositionable diaper closure.

Another more specific object is to provide a self-adhering adhesive that has low or no adhesive buildup to itself.

Another object is to provide a repositionable adhesive.

A more specific object is to provide a repositionable adhesive which is adhesive to itself.

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A further object of the present invention is to provide a method for applying these adhesives without the use of a solvent.

Further advantages and features of the invention, as well as the scope, nature and utilization of the invention will become apparent to those skilled in the art from the following description of the preferred embodiments of the invention.

SUMMARY OF THE INVENTION

The invention provides a low-tack or tack-free adhesive that can be coated onto a backing, generally flexible, to provide an adhesive tape, two pieces of which can bond to each other with excellent resistance to shear forces while still being easily peeled apart, even after prolonged periods of time. When the novel adhesive composition is low-tack, it is a pressure-sensitive adhesive and can have the attributes of the adhesives of the Silver patent, while being more economical to manufacture because it is hot-melt coatable and does not require tiny balls of a stiff pressure-sensitive adhesive or cause the environmental problems of solvent coating methods. Briefly, the novel adhesive comprises a composition of by weight:

from 20 to 80 parts of at least one elastomeric block copolymer selected from styrene/butadiene, styrene/isoprene, and styrene/ethylene-butylene block copolymers, and correspondingly from 80 to 20 parts of tackifying material selected from tackifier resins or blends and blends of tackifier resin with liquid plasticizer oil, which adhesive can be hot-melt coated without the use of solvents and has a composite midblock glass transition temperature (CMTg) from 225 Kelvin to 240 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers and a CMTg from 215 Kelvin to 235 Kelvin when the adhesive is based on styrene/butadiene block copolymer. The CMTg can be calculated using the Fox Equation from the measured Tg of the midblock of the elastomeric block copolymer and the measured Tg of each tackifying resin and liquid plasticizer oil. The Tg for each component is measured using a differential scanning calorimeter such as a DSC-7, manufactured by Perkin-Elmer. The Tg is measured on the second heating run using a scan rate of 20 degrees Centigrade per minute. The first heating run is made up to well above the softening point of the test material. The sample is subsequently quenched to well below the Tg of the material. Antioxidants added to the adhesive are not figured into the calculation of the CMTg.

Fox Equation

$$\frac{\sum_i W_i}{CMTg} = \sum_i \frac{W_i}{Tg_i}$$

where W_i is the weight fraction of component i and Tg_i is the glass transition temperature of component i . Only the midblock portion of the block copolymer is included in the calculation of the CMTg. For a styrene/isoprene block copolymer, the midblock portion is the polyisoprene portion of the molecule.

The tackifier resin or blend, or blend of tackifier resin(s) and liquid plasticizer oil(s) of the novel adhesive can be any of

- solid tackifier resin(s),
- liquid tackifier resin(s),

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- blend of a solid tackifier resin(s) and liquid tackifier resin(s),
- a blend of a solid tackifier resin(s) and liquid plasticizer oil(s), and
- a blend of solid tackifier resin(s), liquid tackifier resin(s), and liquid plasticizer oil(s).

The blends are preferred, because they give a formulator more control over the rheological properties of the adhesive than does the use of a single tackifier resin. For example, when the proportion of elastomeric block copolymer is near the high end (i.e., 55-80 parts) and the CMTg is near the high end (i.e., within 10 Kelvin) of the aforementioned ranges, the novel adhesive tends to have high resistance to shear forces and to be low-tack or tack-free. This type of adhesive will be best suited for use as a self-adhering adhesive. Its low, or no, tack makes it have little or no adhesion to other substrates while its high resistance to shear when attached to itself makes it ideal for a reusable adhesive closure system.

On the other hand, the novel adhesive can be somewhat tacky when the proportion of elastomeric block copolymer is near the low end (i.e., 20-45 parts) and the CMTg is near the high end of those ranges. These adhesives are generally usable as repositionable adhesive tapes, however, they will have a tendency to buildup adhesion over extended periods of time. These adhesives however will still be self-adhering and show the characteristics discussed above.

The least buildup of adhesion to other substrates is realized when both the proportion of elastomeric block copolymer and the CMTg are relatively low. These adhesives are the best suited for use as a repositionable tape on note pads, such as is used in a Post-it™ pad. These tapes, however, will still display self adhesion properties, although generally with lower shear resistance.

Overall, the lower buildup of adhesion to other substrates seems to be primarily related to CMTg while the tendency to build up adhesion to itself seems to be primarily a function of percent polymer concentration. However, these observations are merely generally noted trends, and suitable adhesives for, e.g., self-adhering tape applications or repositionable tapes can be found outside the most likely areas to find such tapes within the invention composition.

In addition to the foregoing components, the adhesive of the invention can incorporate small amounts of other materials commonly used in pressure-sensitive adhesives, e.g. antioxidants such as hindered phenols and hydroquinones, heat stabilizers such as zinc carbamates, ultraviolet stabilizers, fillers, and pigments. Such additional materials can be disregarded in the CMTg calculation.

The adhesive of the invention can be economically converted to tapes by being coated onto backings at high speeds without the use of solvents, or can be coated from solution when that is more convenient. Depending on the backing, the backings can be surface treated to promote adhesion of the adhesive thereto. The resulting tapes can be marketed in strips or in wide sheets and usually have flexible backings for ease of storage, handling, and application. For example, stripes of the novel adhesive can be coated onto paper which is then cut and stacked to form a tablet or note pad of repositionable sheets like the aforementioned POST-IT™ note pads. For such use, the adhesive is preferably somewhat tacky so that sheets of a note pad will

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adhere temporarily to paper and other substrates from which they can later be cleanly removed.

For uses requiring the adhesive to be somewhat tacky, such as for a repositionable note pad, the CMTg can be as low as 220 Kelvin when the adhesive is based on styrene/isoprene or styrene/ethylene-butylene block copolymers which comprise up to 45% by weight of the adhesive.

Whether or not the novel adhesive is low-tack or tack-free, pieces of tape bearing the adhesive have a remarkable ability to form bonds to each other that have excellent resistance to shear forces. In tests, even after four months at ordinary room temperatures, two tapes bearing the novel adhesive separate cleanly between their adhesive layers. The same tapes also separate cleanly after two hours at 37° C. However, low tack adhesives with properties best suited for use as a repositionable adhesive have a tendency to block slightly at above ambient temperatures (e.g., at 37° C.). Therefore, these adhesives would not be as desirable for self-adhering adhesive closures used in close contact with a heated body, such as in a diaper closure system.

In any event, the ability of certain inventive compositions to separate cleanly after 2 hours at 37° C. would make these inventive adhesives well suited for reclosable apparel closures that are used in close proximity to the wearer. Examples of uses for such closure systems include diapers, incontinence devices, surgical gowns, hats or booties, clean room garments, ankle bands, wrist bands or the like. When used, as in reclosable apparel closures, the adhesive can be directly applied to the article or applied as a tape where the side which is permanently attached to the article can have a suitable conventional adhesive. The adhesive would generally be applied as patches on each side of a closure point, e.g., on opposing faces of at least two closure elements that mate to complete the closure. When the two closure elements of the article are brought into contact the adhesive patches will come into contact yielding a resealable closure. The patches can be of a size and arrangement such that they will contact each other over a number of overlapping positions of the closure elements to form an adjustable closure.

For example, the novel adhesive can be used to provide a reclosable disposable diaper by applying a patch of the adhesive to the inner face of each of the corners at the back of a disposable diaper and also to the outer shell where the front of the diaper can be overlapped by the corners when the diaper is wrapped around the waist of a person. The face-to-face contact between those adhesive patches holds the diaper securely in place, but these patches can be easily peeled apart, either to remove or to refasten the diaper.

Where a closure system is used at ambient conditions generally any adhesive composition of the invention can be used with suitable adjustment of the size, shape, and location of the adhesive patches to account for slight variations in the strength of the adhesive bonding strength.

The novel adhesive also can be used to permit labels and masking tapes to be cleanly removed from substrates to which they may be applied. Other useful tape articles of the invention that have flexible backings include reclosable mailing envelopes, resealable bags, adhesive-backed sandpaper and sanding disks, and decals. The novel adhesive also can be marketed in a spray can from which layers can be applied for uses such as temporarily mounting posters or photographs.

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DETAILED DISCLOSURE

Elastomeric block copolymers that are useful in the adhesive of the invention can have any of the common configurations of the block structure including linear diblock and triblock, radial, star, and tapered geometries. Useful elastomers include styrene/isoprene block copolymers such as "Kraton" 1107 and "Kraton" 1111, available from Shell Chemical Co.; "Enichem" SOL T 190, available from Enichem USA; "Quintac" 3421, "Quintac" 3430 and "Quintac" 3530, available from Nippon-Zeon; Finaprene 424, available from Fina Chemical Co.; styrene/butadiene block copolymers such as "Kraton" 1101 and 1102; "Stereon" 840A, available from Firestone Synthetic Latex and Rubber Co., and "Enichem" Sol T 1205 and Sol T 161 C; and styrene/ethylene-butylene block copolymers such as "Kraton" 1657 and 1650.

Tackifier resins that are useful in the novel adhesives include those aliphatic hydrocarbon resins made from the polymerization of a feed stream consisting mainly of unsaturated species containing four to six carbon atoms, such as "Wingtack" 10, "Wingtack Plus", and "Wingtack" 95, available from the Goodyear Tire and Rubber Co.; "Escorez" 1310, available from Exxon Chemical Co., and "Hercotac" RT-95, available from Hercules, Inc.; rosin esters and rosin acids such as "Hercoflex" 400, "Hercoflex" 500, "Foral" 85, "Regalite" 355, and "Permalyn" 305, all available from Hercules, Inc.; mixed aliphatic/aromatic liquid tackifiers such as "Escorez" 2520 available from Exxon Chemical Co.; and polyterpene tackifiers such as "Zonarez" A-25 and "Zonarez" A-100, available from Arizona Chemical Co. and "Piccolyte" HM-85, HM-105, and S-115 available from Hercules, Inc. Also useful are the general class of hydrogenated tackifying resins, including ECR-327, "Escorez" 5380, "Escorez" 5300, "Escorez" 5320, and "Escorez" 5340, all available from Exxon Chemical Co.; "Regalrez" 1018, "Regalrez" 1065, "Regalrez" 1078, "Regalrez" 1094, and "Regalrez" 1126, all available from Hercules Inc.; and "Arkon" P-90, "Arkon" P-100, "Arkon" M-90, and "Arkon" M-100, available from Arakawa Chemical Co.; hydrogenated polyterpene resins such as "Nirez" K-85, "Nirez" K-105, and "Nirez" K-110, available from Reichhold Chemicals, Inc.; and hydrogenated aliphatic and aliphatic/aromatic resins such as ECR-142H and ECR-143H, available from Exxon Chemical Co. Preferred tackifying resins include the aliphatic hydrocarbon resins, the hydrogenated resins, and the polyterpene resins. Especially preferred are the aliphatic hydrocarbon resins.

The liquid plasticizer oils suitable for use in the adhesive of the invention include naphthenic oils such as "Shellflex" 371, available from Shell Chemical Co., paraffinic oils, aromatic oils, and mineral oils such as "Kaydol" oil, available from Witco Chemical Corp. Preferred liquid plasticizers include naphthenic oil and mineral oil.

THE DRAWING

The invention may be more easily understood in reference to the following drawing, in which:

FIG. 1 is a schematic view of a disposable diaper as it would appear while being worn by a person.

The disposable diaper shown in FIG. 1 is a conventional three layer composite including a liquid-permeable user-contacting topsheet 12, a liquid-impermeous outer shell (backsheet) 14, and an absorbent layer there-

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between (not shown). At the back 18 of the diaper are corners 20 that overlap the front of the diaper 22 at corners 28 when the diaper is worn as shown. On the topsheet side of each corner 20 is placed a patch of the inventive adhesive 24. On the outer shell 14 at the front 22 of the diaper are two patches 26 of the inventive adhesive. The patches are placed on the diaper such that they will come into contact when the diaper is worn as shown.

The overlapping portions of the adhesive patches should provide a force to peel generally from 2 to 12N, preferably from 5 to 7N. To provide this peel force resistance and still provide for adjustability, the adhesive patches are placed as is shown in FIG. 1. Each patch would be preferably from 3 to 6 cm in length and from 1.5 to 3 cm in width. The lengthwise directions of the patches are preferably orthogonal to each other. This orientation will provide the greatest degree of adjustability for the preferred patches. Where the patches are so oriented and overlap over an entire width portion, the area of contact will be from 1.75 cm² to 9 cm² for rectilinear shaped patches. Generally this degree of overlap provides sufficient peel resistance for use as a diaper closure system while avoiding excessive or wasteful use of the adhesive.

Testing

Some tapes bearing the adhesive of the invention were subjected to one or more of the following tests:

Probe Tack Value

This is run according to ASTM D-2979 except using a Polyken Probe Tack tester with a polypropylene probe at a 1 cm/second probe speed, a 1 second dwell time, and a 100 gram/cm² load.

90° Peel Value

This is run according to PSTC-5 using a polyethylene substrate to which the test tape was applied using a 2-kg hard rubber roller, one pass in each direction at 30 cm/min. An adhesive which has a 90° Peel Value of from 2 to 8N/25 mm should be useful for making note pads of repositionable sheets like POST-ITTM note pads, because such adhesive-bearing sheets should adhere well to paper and other substrates while being removable without picking fibers, even after prolonged periods of time. When the 90° Peel Value is from 0 to 2N/25 mm, the adhesive would be most useful in the above-described adhesive-to-adhesive diaper closure as these are the least likely to adhere to ordinary packaging materials or to the non-adhesive surfaces of the diaper and hence will not require the use of a protective tape. However, protective tapes can be avoided with even higher peel values. For example, repositionable adhesive formulations may adhere to the diaper parts, however, this may be used to advantage in keeping the diaper folded or at worst be ignored as not affecting tape performance.

180° Peel Value

This is run according to ASTM D-1000 except that the adhesive tape is applied to various substrates using a 2-kg hard rubber roller, one pass in each direction at 30 cm/min, and testing was carried out after less than 20 minutes dwell at ordinary room temperature. The peel rate is 30 cm/min when the substrate is paper and 225 cm/min when the substrate is metal or plastic.

Tapes are also tested after two weeks of accelerated aging at 120° F. (49° C.) and then allowed to cool to room temperature for testing.

180° Dynamic Shear Value

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This value was determined using ASTM Test Method D3528-76 at a crosshead speed of 10 inches (25 cm) per minute.

T-Peel Value

This value was determined using ASTM Test Method D1876-72 at a crosshead speed of 10 inches (25 cm) per minute.

Self-Adhesion Peel Value

with the adhesive layers of two pieces of the same adhesive tape face-to-face, a 2-kg hard rubber roller is applied, one pass in each direction at 30 cm/min. The resulting sandwich is tested for T-peel by ASTM D-1876 at 30 cm/min.

Shear Adhesion Value

A one-inch square (2.54 cm-square) area of a test tape is laid with its adhesive layer against an embossed polyethylene substrate that is used as the backsheet of LUV's brand disposable diapers manufactured by Procter and Gamble and is about 30 μm thick. To enhance the stiffness of the substrate, the polyethylene substrate is laminated to a pressure-sensitive adhesive tape, viz., Release Tape Y-9378 manufactured by 3M Co. On the side opposite the reinforcing tape, the test tape is rolled down onto the polyethylene substrate with a 2-kg hard rubber roller, one pass in each direction at 30 cm/min. The laminated substrate and the test tape are hung vertically in a 40° C. oven for 15 minutes and a 500-gram weight is promptly hung from the test tape. The time for the weight to drop at 40° C. is the Shear Adhesion Value.

The following examples, in which all parts are by weight, are given by way of illustration and are not intended to limit the scope of the invention in any way. Commercial materials used in the examples were:

| ELASTOMERIC BLOCK COPOLYMERS | | MTg |
|------------------------------|---|------|
| "Finaprene" 424 | Styrene/isoprene block copolymer | 215K |
| "Kraton" 1101 | Styrene/butadiene block copolymer | 188K |
| "Kraton" 1107 | Styrene/isoprene block copolymer | 215K |
| "Kraton" 1111 | Styrene/isoprene block copolymer | 215K |
| "Kraton" 1657 | Styrene/ethylene-butylene block copolymer | 215K |
| "Quintac" 3430 | Styrene/isoprene block copolymer | 215K |
| SOLID TACKIFIER RESINS | | Tg |
| "Arkon" P-90 | Hydrogenated hydrocarbon | 309K |
| "Escorez" 1310 | C5 aliphatic | 314K |
| "Escorez" 5300 | Hydrogenated hydrocarbon | 323K |
| "Foral" 85 | Rosin ester | 313K |
| "Piccolyte" HM-105 | Styrenated terpene | 327K |
| "Regalite" 355 | Hydrogenated rosin acid | 318K |
| "Regalrez" 1094 | Hydrogenated hydrocarbon | 310K |
| "Wingtack" 95 | C5 aliphatic | 323K |
| "Wingtack Plus" | C5 aliphatic | 315K |
| "Zonarez" A-100 | Alpha-pinene | 328K |
| LIQUID TACKIFIER RESINS | | |
| ECR-143H | Hydrogenated hydrocarbon | 247K |
| "Escorez" 2520 | Aromatic/aliphatic | 253K |
| "Hercoflex" 500 | Rosin ester | 238K |
| "Wingtack" 10 | C5 aliphatic | 245K |
| "Zonarez" A-25 | Alpha-pinene | 251K |
| LIQUID PLASTICIZER OILS | | |
| "Kaydol" Oil | Mineral oil | 199K |
| "Shellflex" 371 | Naphthenic oil | 209K |
| ANTIOXIDANTS | | |
| "Irganox" 1076 | Hindered Phenol (available from Ciba-Geigy) | |
| "Irganox" 1010 | Hindered Phenol | |

EXAMPLES 1-18

Eighteen adhesive compositions were prepared by dissolving in toluene the components of the formulations given in Table I. One part of "Irganox" 1076 was added to each adhesive composition. Each adhesive solution was 65% by weight of solvent. Tape samples were prepared by coating the adhesive solutions onto a matte-finish cast-polypropylene backing having a thickness of 100 μm . The coating weight of the adhesive after drying at 60° C. for 5 minutes was about 3.5 mg/cm².

Results of testing the tapes of Examples 1-18 are reported in Table II.

TABLE I

| (Compositions for Examples 1-9 in Parts) | | | | | | | | | |
|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Example | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| "Finaprene" 424 | 60 | | | | | | | | |
| "Kraton" 1107 | | 75 | 50 | 65 | 40 | 80 | | | |
| "Kraton" 1111 | | | | | | | 50 | 45 | 80 |
| "Escorez" 2520 | | 23 | 47 | 19 | | | | | |
| "Kaydol" Oil | | | | | | | 31 | 26 | |
| "Shellflex" 371 | | | | | 43 | 7 | | | |
| "Zonarez" A-25 | 32 | | | | | | | | 16 |
| "Arkon" P-90 | | 2 | 3 | 16 | | | | | |
| "Escorez" 1310 | 8 | | | | | | | | |
| "Escorez" 5300 | | | | | | | 19 | 29 | |
| "Wingtack Plus" | | | | | 17 | 13 | | | |
| "Zonarez" A-100 | | | | | | | | | 4 |
| Composite | 235 | 225 | 235 | 235 | 225 | 225 | 225 | 235 | 225 |
| Midblock Tg (Kelvin) | | | | | | | | | |

| (Compositions for Examples 10-18 in Parts) | | | | | | | | | |
|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Example | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| "Kraton" 1101 | | | | | | 20 | 50 | | |
| "Kraton" 1111 | 50 | 70 | | | | | | | |
| "Kraton" 1657 | | | | | | | | 70 | 40 |
| "Quintac" 3430 | | | 75 | 40 | 60 | | | | |
| ECR-143H | | | | | | | | 29 | 58 |
| "Shellflex" 371 | | | | | | 57 | 23 | | |
| "Wingtack" 10 | | | 20 | 56 | 24 | | | | |
| "Zonarez" A-25 | 48 | 16 | | | | | | | |
| "Arkon" P-90 | | | | | | | | 1 | 2 |
| "Piccolyte" HM-105 | | | | | | 23 | 27 | | |
| "Regalrez" 1094 | | | 5 | 4 | 16 | | | | |
| "Zonarez" A-100 | 2 | 14 | | | | | | | |
| Composite | 235 | 235 | 225 | 235 | 235 | 225 | 225 | 225 | 235 |
| Midblock Tg (Kelvin) | | | | | | | | | |

TABLE II

| Example | Probe Tack (N) | 90 Peel Value (N/25 mm) | Shear Adhesion Value (minutes) | Self-Adhesion Peel Value (N/25 mm) |
|---------|----------------|-------------------------|--------------------------------|------------------------------------|
| 1 | 4.2 | 1.4 | 2 | 2.2 |
| 2 | 0.9 | 0.3 | <1 | 2.1 |
| 3 | 4.5 | 1.1 | 2 | 2.2 |
| 4 | 3.3 | 1.4 | 1 | 1.6 |
| 5 | 3.2 | 0.4 | 3 | 1.6 |
| 6 | 1.6 | 1.0 | 1 | 1.0 |
| 7 | 2.2 | 0.7 | 3 | 0.5 |
| 8 | 6.5 | 2.0 | 26 | 0.9 |
| 9 | 0.9 | 0.3 | 16 | 1.2 |
| 10 | 3.5 | 2.0 | 2 | 0.9 |
| 11 | 3.0 | 1.5 | 25 | 1.6 |
| 12 | 1.1 | 0.4 | 1 | 0.8 |
| 13 | 5.9 | 2.7 | 6 | 2.5 |
| 14 | 3.9 | 1.9 | 11 | 2.7 |
| 15 | 2.9 | 0.2 | <1 | 0.2 |
| 16 | 2.6 | 0.8 | <1 | 0.6 |
| 17 | 0.2 | 0.1 | <1 | 2.3 |
| 18 | 2.9 | 0.4 | 11 | 3.4 |

EXAMPLES 19-22

A series of adhesive compositions was made as reported in Table III, and each was dissolved in toluene to a total solids concentration of 25%, with 0.5% of "Irganox" 1010 added to stabilize the adhesive against aging. Each composition was then coated onto a 25 μm thick biaxially oriented poly(ethylene terephthalate) backing and dried to a dry coating weight of about 1.0 mg/cm². The blocks in the star block copolymer used in Examples 20-22 have a linear configuration, with the isoprene chain capped on each end with styrene chains and were prepared in accordance with the procedure outlined in U.S. Pat. No. 4,780,367, the substance of

which is incorporated herein by reference, using a divinylbenzene catalyst to yield a polymer with 16.8% styrene and the remainder predominately isoprene. Results of testing each of Examples 19-22 for 180° Peel Value are reported in Table IV.

TABLE III

| (Compositions for Examples 19-22) | | | | |
|--|------|------|------|-------|
| Material | 19 | 20 | 21 | 22 |
| "Kraton" 1107 | 80 | | | 17 |
| Star block polymer of styrene/isoprene | | 35 | 20 | 25.5 |
| "Wingtack Plus" | 17.4 | 0.3 | 1.7 | 0.3 |
| "Wingtack" 10 | 2.6 | 64.7 | 78.3 | 57.2 |
| CMTg | 230 | 235 | 240 | 232.5 |

TABLE IV

| (180° Peel Value in OZ/g) | | | | |
|---------------------------|-----|-----|-----|-----|
| Substrate | 19 | 20 | 21 | 22 |
| Paper | 1.7 | 3.2 | 5.0 | 2.4 |
| After aging | 4.1 | 8.9 | 6.6 | 7.0 |
| Stainless Steel | 16 | 11 | 25 | 17 |

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TABLE IV-continued

| Substrate | (180° Peel Value in OZ/g) | | | |
|-------------|---------------------------|----|----|----|
| | 19 | 20 | 21 | 22 |
| After aging | 31 | 25 | 35 | 28 |
| BOPP | 19 | 13 | 24 | 20 |
| After aging | 18 | 19 | 26 | 20 |
| PET | 28 | 18 | 23 | 22 |
| After aging | 28 | 29 | 35 | 27 |

Paper = ordinary bond copypaper

BOPP = biaxially oriented polypropylene

PET = biaxially oriented poly(ethylene terephthalate)

The data reported in Table IV show that each of the adhesives of Examples 19-22 has low adhesion to paper and other substrates and has low adhesion build-up with time evidenced by low adhesion after accelerated aging for two weeks at 49° C. This demonstrates that the adhesive of any of Examples 19-22 should be a suitable substitute, in repositionable note pads, for the adhesive of the above-cited Silver patent, even though these are not preferred examples of such substitute adhesives.

EXAMPLE 23

A handsread of 50% solution in toluene of 70 parts of "Kraton" 1657 and 30 parts of "Res" D-2084 was pulled onto biaxially oriented poly(ethylene terephthalate) film having a thickness of 2.5 μ m. The dried coating weight was about 24 g/m². This adhesive had:

CMTg=238 Kelvin

180° Dynamic Shear Value to itself=588N/cm²

T-Peel Value=6.5N/25 mm

Comparative Examples A-G

A series of tapes were made in the same way as the tapes of Examples 1-18 except using adhesive compositions indicated in Table V. Some of the adhesive compositions were as taught in the prior art as follows:

| Comparative Example | Adhesive as Taught in |
|---------------------|--|
| F | Sample 10 of Example III in U.S. Pat. No. 3,954,692 (Downey) |
| G | Example 4 of U.S. Pat. No. 3,932,328 (Korpmann) |

TABLE V

(Compositions in Parts)

| Comparative Example | A | B | C | D | E | F | G |
|----------------------|-----|-----|-----|-----|-----|-----|-----|
| "Finaprene" 424 | 40 | | | | | | |
| "Kraton" 1107 | | 50 | | | | 100 | 100 |
| "Quintac" 3430 | | | 40 | 30 | 40 | | |
| "Wingtack" 10 | | | | 26 | 11 | | 40 |
| "Zonarez" A-25 | 22 | | | | | | |
| "Kaydol" Oil | | | 6 | | | 20 | |
| "Shellflex" 371 | | 8 | | | | | |
| "Wingtack" 95 | | | | | | 100 | 100 |
| "Escorrez" 1310 | 38 | | | | | | |
| "Regalite" 355 | | | 54 | | | | |
| "Regalrez" 1094 | | | | 44 | 49 | | |
| "Wingtack Plus" | | 42 | | | | | |
| Composite | 258 | 250 | 262 | 260 | 260 | 254 | 254 |
| Midblock Tg (Kelvin) | | | | | | | |

Testing of comparative example A-G is reported in Table VI.

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TABLE VI

| Example | Probe Tack (N) | 90° Peel Value (g/25 mm) | Shear Adhesion Value (minutes) | Self-Adhesion Peel Value (N/25 mm) |
|---------|----------------|--------------------------|--------------------------------|------------------------------------|
| A | 13 | 7.3 | >1000 | 15 |
| B | 10 | 4.6 | >1000 | 12 |
| C | 10 | 13.6 | >1000 | 12 |
| D | 9 | 9.3 | >1000 | 18 |
| E | 12 | 8.0 | >1000 | 17 |
| F | 11 | 4.9 | >1000 | 18 |
| G | 10 | 7.8 | >1000 | 16 |

As indicated in Tables II and VI, comparative Examples A through G exhibit tack, peel, shear and self-adhesion values that are substantially greater than Example 1 through 18 and are typical of conventional pressure-sensitive adhesives that are based on elastomeric block copolymers.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A low-tack or no-tack adhesive consisting essentially of a composition of by weight:

from 20 to 80 parts of at least one elastomeric block copolymer selected from the group consisting of styrene/butadiene and styrene/isoprene block copolymers, and

correspondingly from 80 to 20 parts of tackifying material selected from the group consisting of tackifier resin and a blend of tackifier resin and liquid plasticizer oil, wherein the tackifier comprises 0 to 35 parts of a solid tackifier resin and from 0 to 80 parts of a liquid tackifying resin or plasticizing oil, and wherein the tackifier resin is selected from the group consisting of aliphatic hydrocarbon resins from the polymerization of unsaturated species with four to six carbon atoms, rosin esters and acids, aliphatic/aromatic liquid tackifiers, polyterpene tackifiers, hydrogenated tackifying resins, hydrogenated polyterpene resins and hydrogenated aliphatic and aliphatic/aromatic resins, and the liquid plasticizer oils are selected from the group consisting of mineral oil, naphthenic oil, paraffinic oil, and

aromatic oils, and mixtures thereof, which adhesive has a composite midblock glass transition temperature (CMTg) from 225 Kelvin to 240 Kelvin when the adhesive is based on styrene/isoprene block copolymers and a CMTg from 215 Kelvin to 235 Kelvin when the adhesive is based on styrene/butadiene block copolymers to provide an adhesive having no tack or low tack, which adhesive has a 90 degree peel value (as herein defined) of 0.1 to 2.7N/25 mm and a self-adhesion value (as herein defined) of from 0.2 to 3.4N/25 mm.

2. An adhesive as defined in claim 1 and having a 90 degree Peel Value (as herein defined) of 0.1 to 2N/25 mm.

3. An adhesive as defined in claim 1 wherein the elastomeric block copolymer has a configuration selected from the group consisting of linear diblock and triblock, radial, star, and tapered block geometries.

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4. An adhesive as defined in claim 1 and containing both a tackifier resin and a liquid plasticizer oil.

5. An adhesive as defined in claim 1 and comprising from 55 to 80 parts by weight of the elastomeric block copolymer.

6. An adhesive as defined in claim 5 wherein the CMTg is within 10° Kelvin of the top of an aforementioned range.

7. An adhesive as defined in claim 1 and comprising

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from 20 to 45 parts by weight of the elastomeric block copolymer.

8. An adhesive as defined in claim 7 wherein the CMTg is within 10 Kelvin of the bottom of an aforementioned range, and the adhesive is a pressure-sensitive adhesive.

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United States Patent [19]**Mertens et al.**[11] **Patent Number:** **5,618,062**[45] **Date of Patent:** **Apr. 8, 1997**[54] **NOTE OR NOTE PAD PREPARATION METHOD**[75] **Inventors:** Timothy A. Mertens, Cottage Grove;
Mark S. Vogel, Maplewood, both of Minn.[73] **Assignee:** Minnesota Mining and Manufacturing Company, St. Paul, Minn.[21] **Appl. No.:** 373,585[22] **Filed:** Jan. 17, 1995**Related U.S. Application Data**[63] **Continuation-in-part of Ser. No. 973,039, Nov. 9, 1992, Pat. No. 5,382,055.**[51] **Int. Cl.⁶** B42D 15/00[52] **U.S. Cl.** 283/67; 283/117; 412/1; 412/10; 462/67[58] **Field of Search** 283/67, 117; 412/1, 412/10; 462/67; 428/40[56] **References Cited****U.S. PATENT DOCUMENTS**

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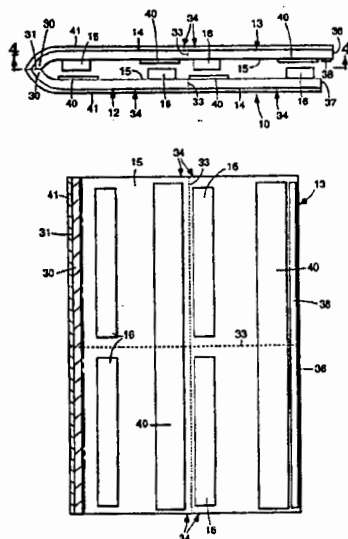
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Primary Examiner—Frances Han**Attorney, Agent, or Firm**—Gary L. Griswold; Walter N. Kirn; William L. Huebsch[57] **ABSTRACT**

A method for making custom printed notes or note pads. One or more sheet assemblies are provided which have first and second sheets and a pattern of pressure-sensitive adhesive on the rear major surface of each of the sheets that contacts and is releasably adhered to the rear major surface of the other sheet only in nonadhesive areas. Indicia is printed on the front major surfaces of the sheets using a conventional copy machine. The sheets can either be cut along predetermined lines to form the custom printed notes, or the sheets of a plurality of such printed sheet assemblies can be separated, stacked to adhere the patterns of pressure-sensitive adhesive on the rear major surfaces of the sheets to the front major surfaces of the sheets with the edges of the sheets in a predetermined orientation with respect to each other, and the stacked sheets can be cut along predetermined lines to form custom printed note pads.

17 Claims, 6 Drawing Sheets

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U.S. Patent

Apr. 8, 1997

Sheet 1 of 6

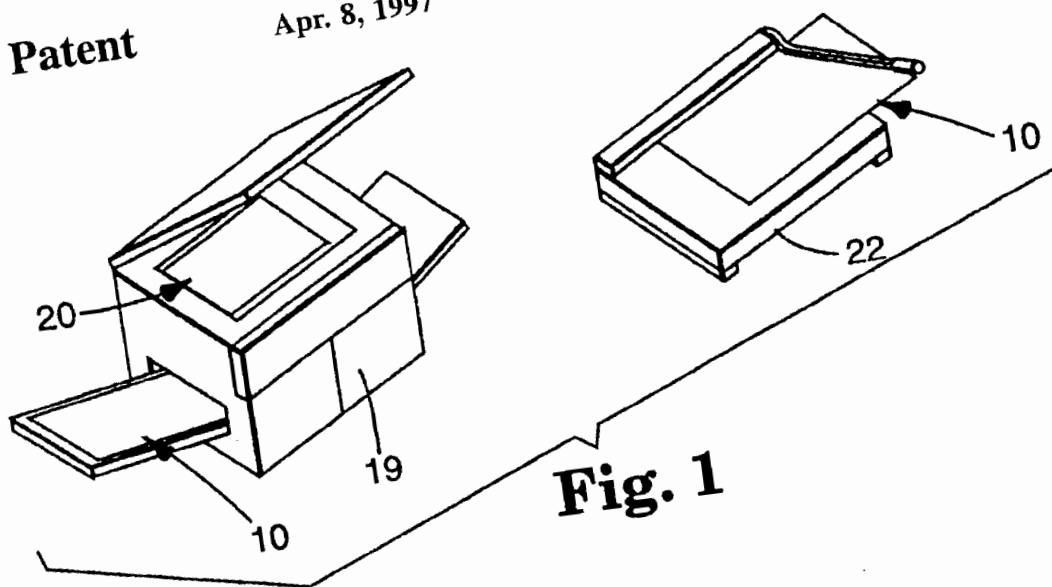


Fig. 1

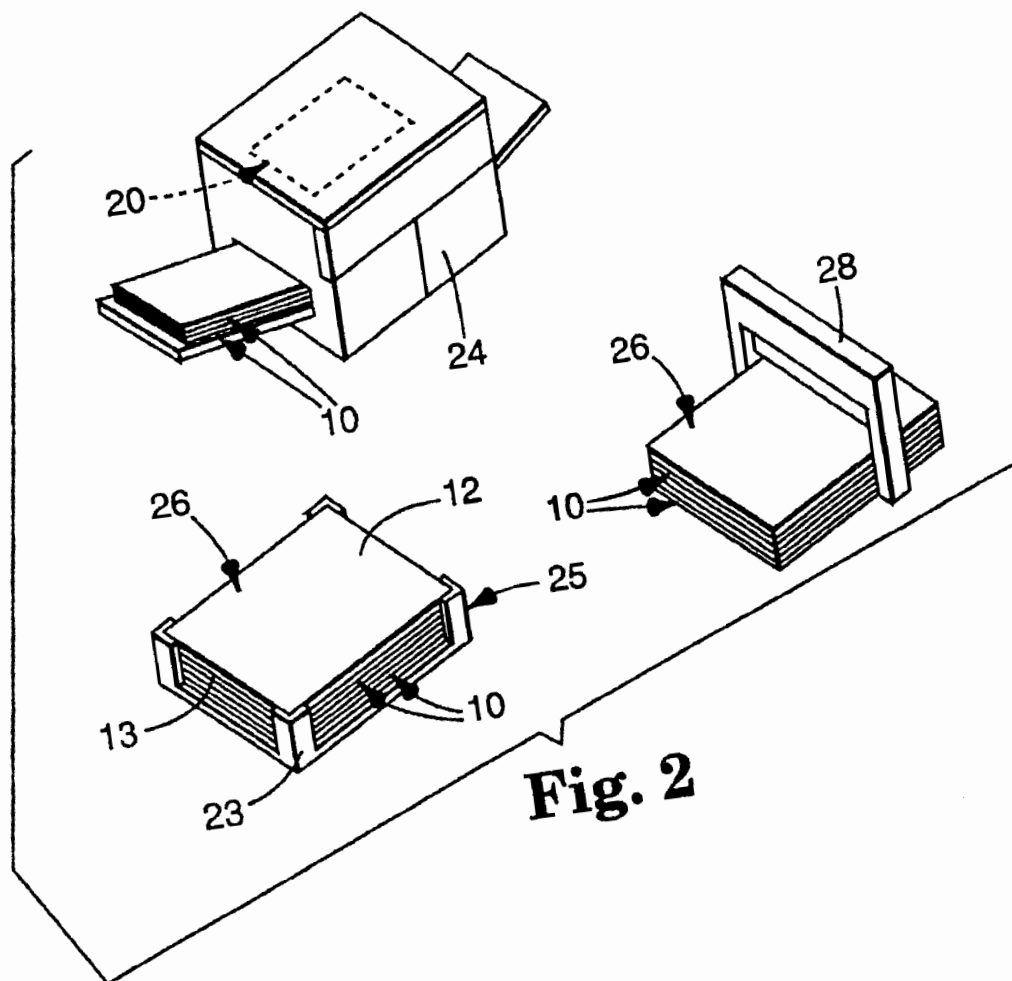


Fig. 2



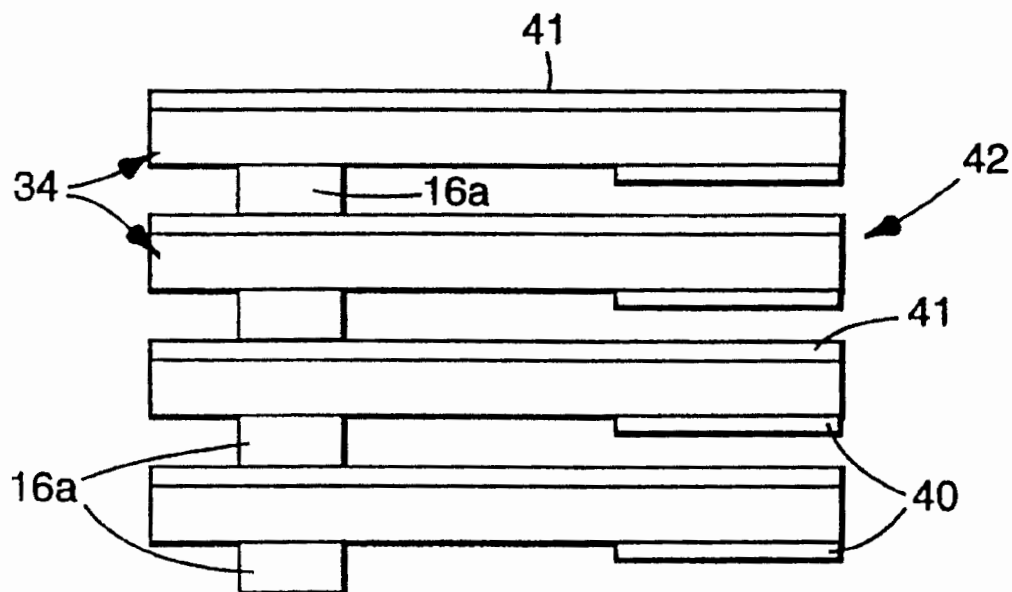


Fig. 5

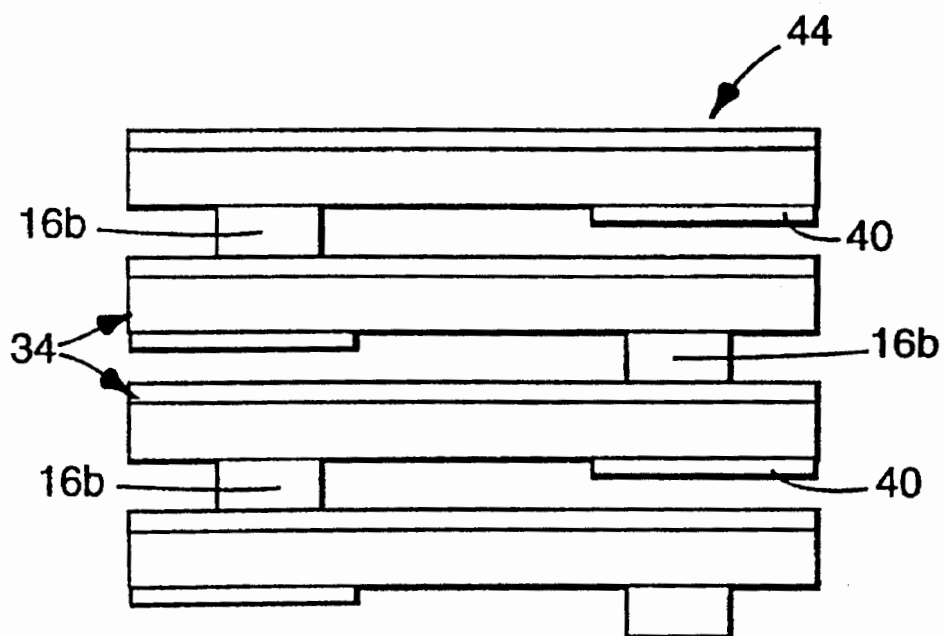


Fig. 6

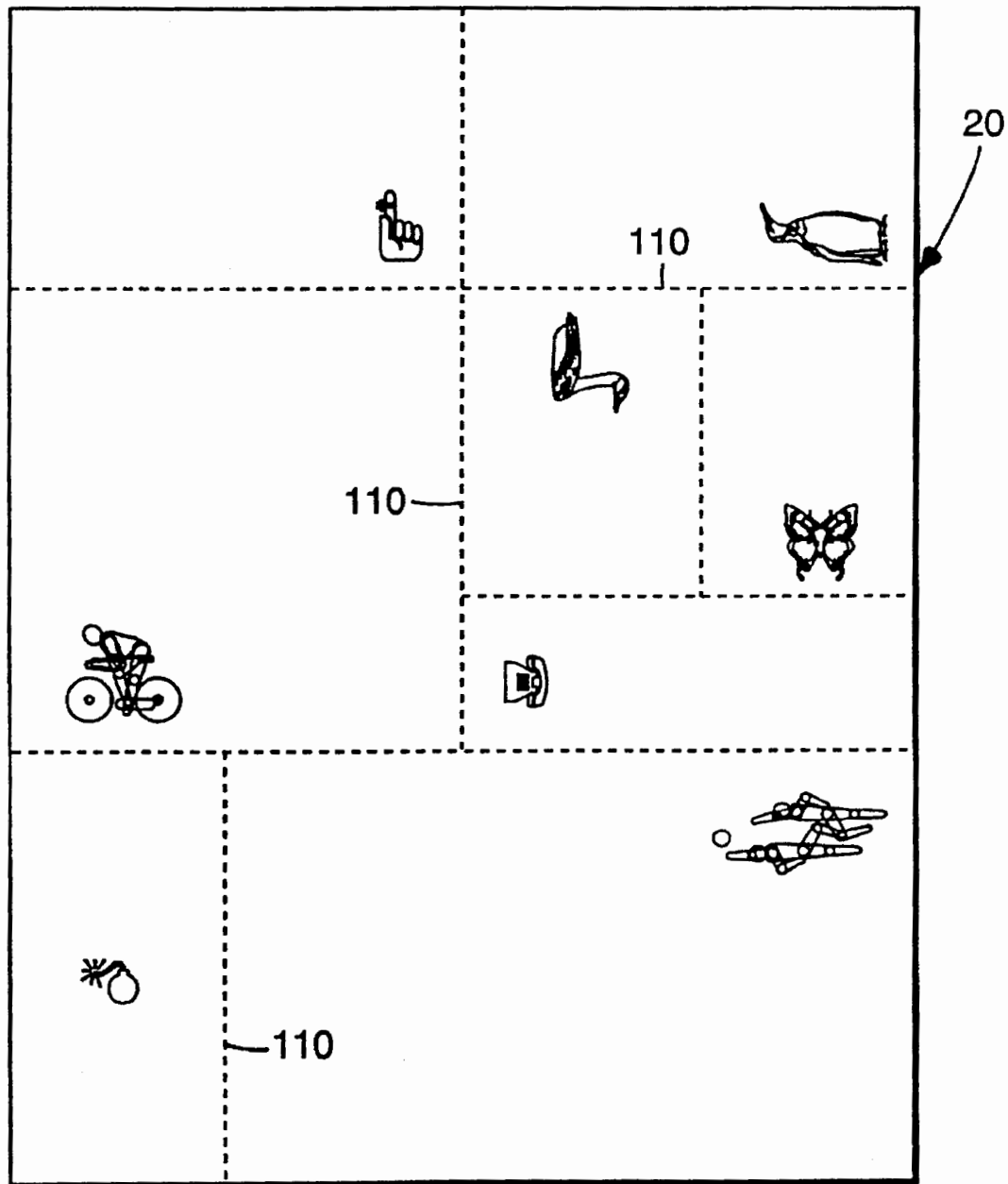


Fig. 7

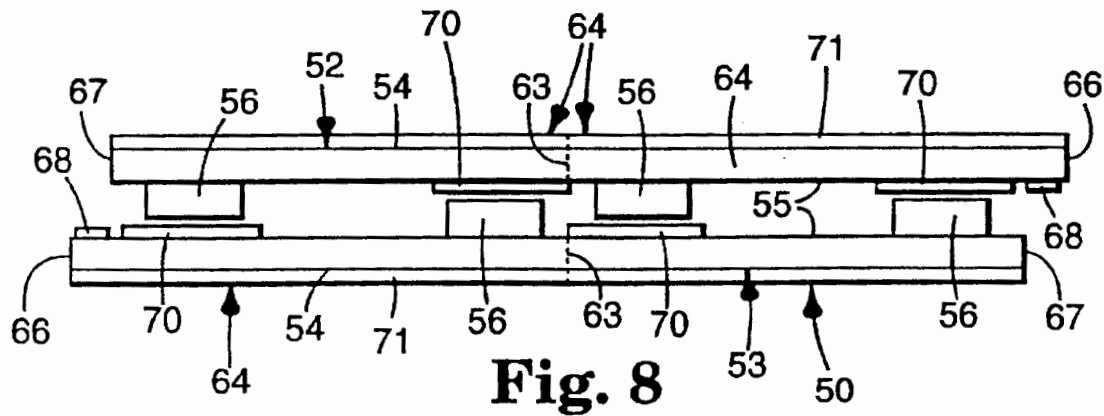


Fig. 8

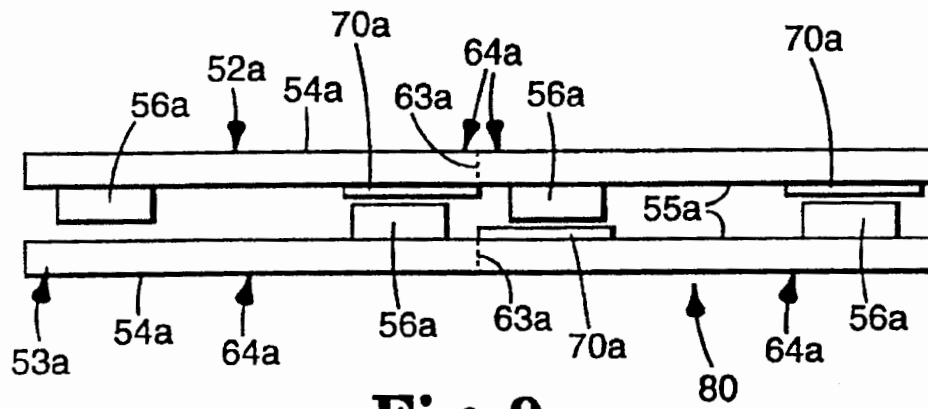


Fig. 9

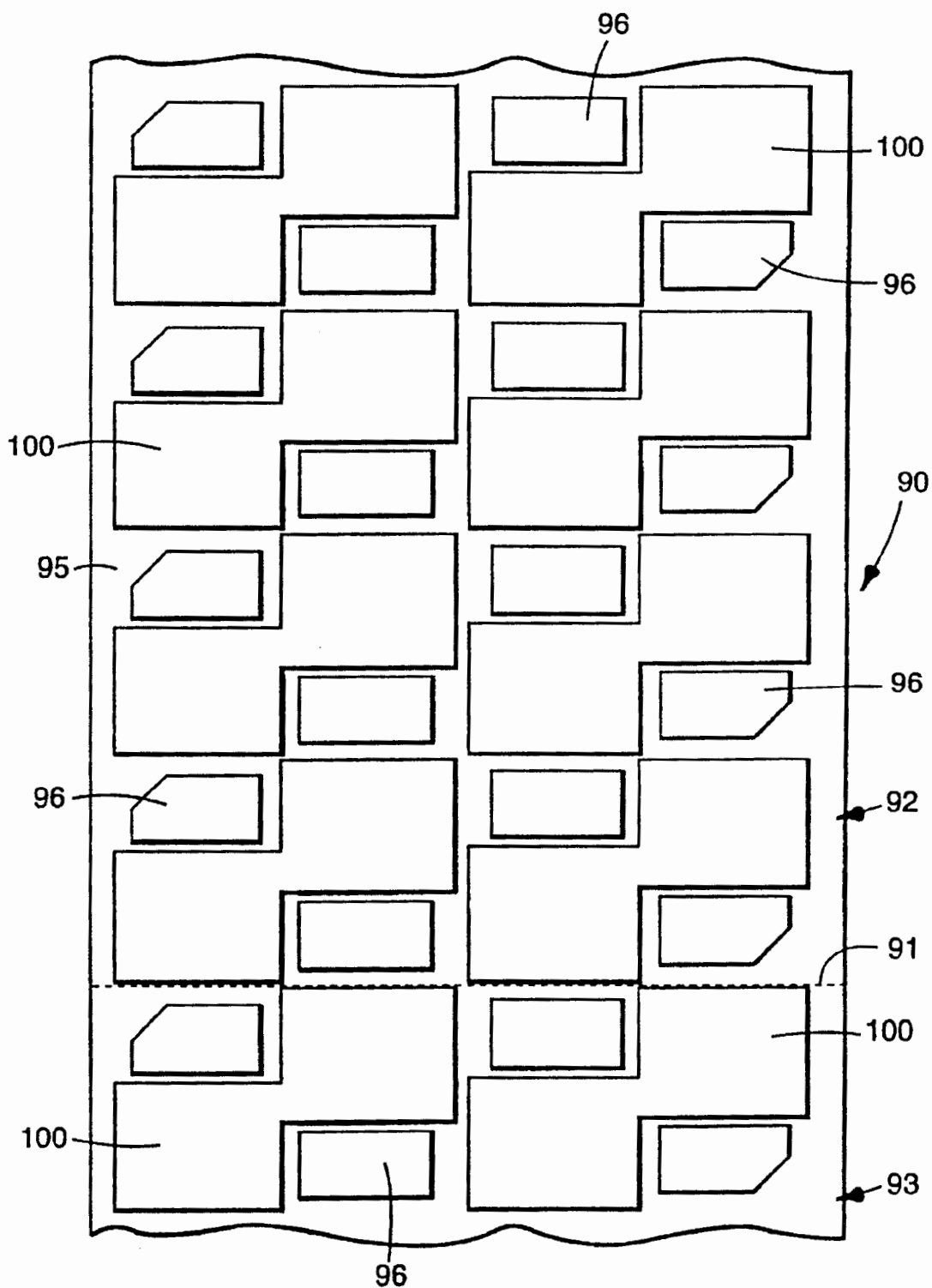


Fig. 10

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ing from about 10-85% of the area over which adhesive is applied, so as to achieve an adhesion to polyester film on the order of 8-80 grams per centimeter width, whereby said adhesive product can be adhered to newsprint, allowed to remain in contact therewith for two 5

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weeks at room temperature and then removed without visibly damaging the newsprint and; wherein said adhesive islands occupy from about 20 to about 60% of the area over which the adhesive is applied.

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NOTE OR NOTE PAD PREPARATION METHOD

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. patent application Ser. No. 07/973,039, filed Nov. 9, 1992, now U.S. Pat. No. 5,382,055 issued Jan. 17, 1995.

TECHNICAL FIELD

The present invention relates to methods for printing indicia on paper sheets of the type having a narrow strip of pressure-sensitive adhesive adjacent one edge on its rear side by which the sheets can be adhered to a substrate, making pads of such sheets, and to sheet materials used in such printing methods.

BACKGROUND ART

A well known note pad comprises a stack of paper sheets, each having a narrow strip of low-tack pressure-sensitive adhesive adjacent one edge on its rear side by which the sheets can be temporarily adhered to substrates such as documents or other articles (often for message-bearing purposes), by which strip of adhesive the sheet are adhered together in the pad. In one pad configuration, all of the strips of adhesive are along one side of the note pad, whereas in another pad configuration the adhesive strip on each successive sheet in the pad is along the opposite side of the pad as is illustrated in U.S. Pat. No. 4,416,392. Note pads in both of these configurations are currently being marketed under the trademark "Post-it" by Minnesota Mining and Manufacturing Company, St. Paul, Minn. Some such note pads have printed indicia (e.g., a printed message and/or picture and/or decoration) on each sheet, however, heretofore, such indicia has been printed on sheet material from which the note pads are formed by the manufacturer of the note pads, and printing of indicia on such note pads has only been economically feasible when a large amount of such note pads are produced.

DISCLOSURE OF INVENTION

The present invention provides a method, and a sheet assembly used in that method, by which an individual or a small custom printing company can economically prepare a small amount of notes or note pads having pressure-sensitive adhesive on a rear surface and custom printed indicia (e.g., printed messages and/or decorations and/or pictures and/or indicia that make the notes usable as flags, labels or forms) on the front surfaces of all or some of the sheets using conventional printing means including electrophotography through laser printers, conventional office copiers, lithography, flexography, or the like.

The method for making custom printed notes or note pads according to the present invention utilizes one or more novel sheet assemblies, each of which has first and second sheets and layers of pressure-sensitive adhesive in a predetermined pattern on the rear major surface of each of the sheets that contact and are releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas. Indicia are printed on the front major surfaces of the sheets using conventional printing means of the type described above. The sheets can then either be separated along predetermined planes normal to and extending across the major surfaces of the sheets to form the custom printed notes, or the sheets of

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a plurality of such printed sheet assemblies can be separated, stacked to adhere the layers of pressure-sensitive adhesive on the rear surfaces of the sheets to the front surfaces of other sheets in the stack with the layers of adhesive on the sheets in a predetermined orientation with respect to each other; and the stacked sheets can be separated along predetermined planes normal to and extending across the major surfaces of the sheets to form the custom printed note pads.

The adhesive used in the layers of pressure-sensitive adhesive can be a low-tack pressure-sensitive adhesive (e.g., comprising tacky, elastomeric copolymer microspheres) in which case the nonadhesive bearing areas on the rear surfaces of the sheets to which the layers of adhesive are adhered in the sheet assemblies and the front surfaces of the sheets can be free of release coating; or a conventional more aggressive pressure-sensitive adhesive can be used in which case the sheet assembly can include a release coating on those nonadhesive bearing areas to afford separation of the sheets of the sheet assembly after printing, and can further include a release material on the front major surface of one or both of the sheets (e.g., an indicia-receptive polymer) which affords separation of the sheets from the stack.

The sheet assembly can further include orientation indicating means for indicating the orientation of the layers of adhesive on the sheet assembly between the sheets to afford printing in the proper orientation on the sheet, to facilitate separation of the sheets in the sheet assembly, and to facilitate subsequent stacking of the sheets in a desired orientation. The orientation indicating means can be visible, tactile, olfactory, auditory, or tasteable, and can, for examples, be provided by (1) a portion of one sheet adjacent one of its edges extending past the adjacent edge of the other sheet, (2) printed marks on the front surface of one or both of the sheets or printed marks on such a projecting portion, (3) embossed tactile markings on one or both of the sheets, (4) scented portions of one or both of the sheets, (5) coatings on one or both of the sheets that can be tasted, or (6) rough portions on one or both of the sheets that cause a raspy sound when the edge of an object such as a fingernail is rubbed over it. Providing more than one of such orientation means could be useful to accommodate possible users with certain physical handicaps.

The sheets in the sheet assembly can be of any conventional material (e.g., conventional, bond, or clay-coated paper, opaque or translucent polymeric material, or the carbonless paper sold under the trademark "Scotchmark" by Minnesota Mining and Manufacturing Company, St. Paul, Minn. which is paper containing structures such as micro-encapsulated chemicals that will form an image on the paper when pressure is applied to the paper so that, for example, the capsules are broken by the pressure to release the image forming chemical). The sheets in the sheet assembly can be entirely separate and attached only by the layers of adhesive, or can be made from a larger sheet or web in such a way that they are attached along adjacent edges and have a path of weakness along those attached edges. By "Path of weakness" we mean any weakening of the sheet material along a line that permits the sheets to fold or tear apart along that line while providing sufficient integrity so that the sheets do not separate along that line while they are being imprinted. A suitable path of weakness can be provided by forming spaced perforations through the sheet, crushing the sheet, chemical treatment to reduce the thickness and/or the strength of the sheet, grooves formed by control-depth cuts, or the like.

BRIEF DESCRIPTION OF DRAWING

The present invention will be further described with reference to the accompanying drawing wherein like refer-

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ence numerals refer to like parts in the several views, and wherein:

FIG. 1 is a schematic view of a first embodiment of a method according to the present invention for making custom printed notes;

FIG. 2 is a schematic view of a second embodiment of a method according to the present invention for making custom printed note pads;

FIG. 3 is an edge view of a sheet assembly according to the present invention that can be used in the methods illustrated in FIGS. 1 and 2;

FIG. 4 is a reduced sectional view taken approximately along line 4—4 of FIG. 3;

FIGS. 5 and 6 are edge views of optional forms of note pads made by the method of FIG. 2;

FIG. 7 is a plan view of a pattern sheet that can be used in the methods illustrated in FIGS. 1 and 2; and

FIGS. 8 and 9 are edge views of second and third alternate embodiments of sheet assemblies according to the present invention that can be used in the methods illustrated in FIGS. 1 and 2;

FIG. 10 is a fragmentary view illustrating an alternative pattern for layers of adhesive that can be used on a sheet assembly used in the methods illustrated in FIGS. 1 and 2.

DETAILED DESCRIPTION

Referring now to FIG. 1 of the drawing, there is schematically illustrated a first embodiment of a method according to the present invention for making a small amount of custom printed notes. Generally that method comprises the steps of (1) providing a sheet assembly such as the sheet assembly 10 illustrated in FIGS. 3 and 4 which comprises first and second sheets 12 and 13 each having major front and rear surfaces 14 and 15, and spaced layers 16 of pressure-sensitive adhesive in a predetermined pattern on the rear surface 15 of each of the sheets 12 or 13 contacting and releasably adhering to the rear surface 15 of the other sheet 12 or 13 only in nonadhesive bearing areas of that rear surface 15 that are recessed with respect to the layers 16 of pressure-sensitive adhesive (such contact not being illustrated in FIG. 3); (2) printing indicia on at least one of the front surfaces 14 of the sheets 12 and 13 in the sheet assembly 10 using a printing device such as a conventional office copy machine 19 for which there has been prepared an appropriate pattern sheet to be copied, such as the pattern sheet 20 illustrated in FIG. 7; (3) and separating portions of the sheets 12 and 13 along predetermined planes normal to and extending across the major surfaces 14 and 15 of the sheets 12 and 13 to form the custom printed notes (each separated portion having two such notes releasably adhered together by the parts of the layers 16 of adhesive on the notes), which separating could be done by tearing the sheets 12 and 13 along patterns of weakness between the sheet portions (if such patterns of weakness are provided), or by cutting with a conventional scissors, but as illustrated is being done by cutting with a conventional office paper cutter 22. This method allows a person having the sheet assembly 10, a pattern sheet such as the pattern sheet 20 which the person could prepare with custom indicia, and access to a copy machine 19 to easily make a small number of notes having pressure-sensitive adhesive on their back surfaces which are printed with indicia of that persons choosing on their front surfaces.

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Referring now to FIG. 2 of the drawing, there is schematically illustrated a second embodiment of a method according to the present invention for making custom printed note pads. Generally that method comprises the steps of (1) providing a plurality of sheet assemblies such as the sheet assembly 10 illustrated in FIGS. 3 and 4, each of which sheet assemblies 10 comprises first and second sheets 12 and 13 each having major front and rear surfaces 14 and 15 and layers 16 of pressure-sensitive adhesive in a predetermined pattern on the rear surface 15 of each of the sheets 12 and 13, the layers 16 of pressure-sensitive adhesive on the rear major surface 15 of each of the sheets 12 or 13 in each of the sheet assemblies 10 contacting and being releasably adhered to the rear surface 15 of the other sheet 12 or 13 only in nonadhesive bearing areas that are recessed with respect to the layers 16 of pressure-sensitive adhesive; (2) printing indicia on at least one and usually both of the front surfaces 14 of the sheets 12 and 13 in at least some and usually all of the sheet assemblies 10 (which indicia could be different on different sheet assemblies 10) using a printing device 24 of the type often found in small printing shops (e.g., a conventional office copy machine for which an appropriate printing pattern is provided by a pattern sheet that is copied such as the pattern sheet 20 illustrated in FIG. 7, electrophotography through laser printers for which an appropriate printing pattern is provided by digital electronic signals from a computer or the like, or, lithography or flexography for which an appropriate printing pattern is provided by printing plates); (3) separating the sheets 12 and 13 in the sheet assemblies 10 after the printing step (not shown); (4) stacking the separated sheets 12 and 13 (e.g., in a stacking frame 25 which aligns adjacent edges of the sheets 12 and 13 adjacent one lower corner 23 of the frame as illustrated) to adhere the layers 16 of pressure-sensitive adhesive on the rear surfaces 15 of the sheets 12 and 13 to the front surfaces 14 of the other sheets 12 and 13 in the stack to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation with respect to each other; and (5) separating the stacked sheets 12 and 13 along predetermined planes normal to and extending across the major surfaces 14 and 15 of the sheets 12 and 13 in the master stack 26 to form the custom printed note pads; which separating could be done by tearing the sheets 12 and 13 along patterns of weakness between the sheet portions (if such patterns of weakness are provided and the note pads are made using very few sheet assemblies 10), or by cutting with a conventional office paper cutter, but, as illustrated, is being done by cutting with a conventional guillotine cutter 28 of a type often found in small printing companies. This method is particularly useful for persons or companies that provide small printing and copying services to the public (e.g., the companies having the trademark "Insty-prints") so that they can form a small amount of custom printed note pads for customers.

The sheets 12 and 13 of the sheet assembly 10 illustrated in FIGS. 3 and 4 are half portions of a large sheet or web and joined along adjacent edges 30, with a path of weakness 31 provided by spaced perforations along those joined edges 30 so that the sheets 12 and 13 are folded and can be torn apart along that path of weakness 31, while the strength of attachment between the sheets 12 and 13 across that path of weakness 31 prevents the sheets 12 and 13 from separating along their joined edges 30 while they are being printed. Optionally, as illustrated, the sheets 12 and 14 can also be perforated to have additional paths of weakness 33 along planes normal to and extending across the surfaces 14 and 15 of the sheets 12 and 13 so that the sheets 12 and 13 can be

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manually separated into segments 34. The sheets 12 and 13 have adjacent terminal edges 36 and 37 respectively that are opposite the joined edges 30 and between which separation of the sheets 12 and 13 may be initiated. The layers 17 of pressure-sensitive adhesive on the sheets 12 and 13 are in the form of spaced strips of the adhesive that extend transversely of the sheets 12 and 13 parallel to the edges 30, 36 and 37 with each strip being adjacent and extending along an edge of a portion 34 of the sheet that will be formed by separating the sheets 12 and 13 along the paths of weakness 31 and 33.

The sheet assembly 10 is illustrated in FIGS. 3 and 4 with release coatings 40 on the nonadhesive bearing areas of the rear surfaces 15 of the sheets 12 and 13. The release coatings 40 are also in strips, are slightly wider than the strips 16 of adhesive, and extend transversely of the sheets 12 and 13 parallel to the edges 30, 36 and 37 with each strip release coating 40 being adjacent and extending along an edge of a portion 34 of the sheet 12 and 13 that will be formed by separating the sheets 12 and 13 along the paths of weakness 31 and 33, and in a position such that when the rear surfaces 15 of the sheets are placed face to face as illustrated in FIG. 3, the strip layers 16 of adhesive will contact and will be generally centered on the strip release coatings 40. Also, as illustrated, the entire front surface 14 of each of the sheets 12 and 13 is coated with a release coating 41. The illustrated release coatings 40 on the rear surfaces 15 and the release coatings 41 on the front surface 14 of the sheets 12 and 13 are not needed when the layers 16 of adhesive are of low-tack or repositionable adhesive (e.g., the low-tack adhesives based on tacky, elastomeric copolymer microspheres disclosed in U.S. Pat. Nos. 3,961,140 and 3,857,731). The use of the release coatings 40 and 41 allows the use of layers 16 of pressure-sensitive adhesive that are more aggressive or permanent than repositionable adhesive. Suitable release coatings 40 and 41 are materials and treatments which provide a controlled separation force from the layers 16 of adhesive. The release coating 41 should comprise an indicia-receptive material or polymer to facilitate printing on the front surfaces 14 of the sheets 12 and 13. Typical release coatings 40 and 41 include silicones, acrylates, chrome complexes, and fluorochemicals. Even with layers 16 of aggressive pressure-sensitive adhesive the release coatings 40 and 41 might not be required if the sheets 12 and 13 are of a material, or are impregnated with a material, from which the layer 16 of adhesive readily releases.

The sheets 12 and 13 are generally of flat, flexible material including, but not limited to, plain or bond paper, clay coated paper, films, foils, nonwoven materials, opaque or transparent polymeric materials and carbonless paper, and could have double layers so that they form pouches or envelopes.

The sheets 12 and 13 can be stacked as described above to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation directly above each other which can result in note pads such as a note pad 42 illustrated in FIG. 5 which has a portion 16a of one of the layers 16 of adhesive along a corresponding edge of each portion 34 of one of the sheets 12 or 13 in the pad 42; or the sheets 12 and 13 can be stacked to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation spaced from above each other which can result in note pads such as a note pad 44 illustrated in FIG. 6 in which each successive portion 34 of one of the sheets 12 or 13 in the pad has a portion 16b of one of the layers 16 of adhesive along an opposite edge of the pad 44.

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The sheet assembly 10 also includes indicating means for indicating the orientation of the layers 16 of pressure-sensitive adhesive between the sheets 12 and 13 of the sheet assembly 10. As illustrated that indicating means for indicating the orientation of the layers 16 of pressure-sensitive adhesive is provided in two ways, (1) by a portion of the second sheet 13 adjacent its edge 36 extending past the adjacent edge 37 of the first sheet 12, and (2) by providing a mark or indicia 38 on the projecting portion of the second sheet 13. With appropriate instructions (which may be provided by the indicia 38) a user can be made aware of the orientation of the layers 16 of adhesive with respect to the edges of the sheets 12 and 13 in the sheet assembly 10 so that he can print the indicia on the front surfaces 14 of the sheets 12 and 13 in the proper orientation with respect to those layers 16 of adhesive. As an alternative to the indicating means illustrated, either a projecting portion of one of the sheets 12 or 13 or a mark or indicia such as the indicia 38 illustrated may be used alone, or the sheet assembly 10 could be made without any such indicating means.

FIG. 8 illustrates a second embodiment of a sheet assembly 50 according to the present invention that could be used in the methods illustrated in FIGS. 1 and 2. Like the sheet assembly 10 illustrated in FIGS. 3 and 4, the sheet assembly 50 illustrated in FIG. 8 comprises first and second sheets 52 and 53 each having major front and rear surfaces 54 and 55, and spaced layers 56 of pressure-sensitive adhesive in the same predetermined pattern on the rear surface 55 of each of the sheets 52 and 53, the layers 56 of pressure-sensitive adhesive in the predetermined pattern on the rear surface 55 of each of the sheets 52 or 53 contacting and releasably adhering to the rear surface 55 of the other sheet 52 or 53 only in nonadhesive bearing areas 58 of that rear surface 55 that are recessed with respect to the layers 56 of pressure-sensitive adhesive (such contact not being illustrated in FIG. 8). Unlike the sheets 12 and 13 of the sheet assembly 10 illustrated in FIGS. 3 and 4, the sheets 52 and 53 are totally separate rather than being joined along one edge, and each of the sheets has corresponding opposite edges 66 and 67. Optionally, as illustrated and like the sheets 12 and 13, the sheets 52 and 53 can also be perforated to have paths of weakness 63 along planes normal to and extending across the surfaces 54 and 55 of the sheets 52 and 53 so that the sheets 52 and 53 can be manually separated into segments 64; and the sheet assembly 50 can have release coatings 70 on the nonadhesive bearing areas of the rear surfaces 55 of the sheets 52 and 53 (which coatings 70 are not needed if the adhesive is low tack) which coatings 70 are also in strips, are slightly wider than the strips 56 of adhesive, and extend transversely of the sheets 52 and 53 parallel to the edges 66 and 67 with each strip release coating 70 being adjacent and extending along an edge of a portion 64 of the sheet 52 and 53 that will be formed by separating the sheets 52 and 53, and in a position such that when the rear surfaces 55 of the sheets are placed face to face as illustrated, the strip layers 56 of adhesive will contact the strip release coatings 70 in a generally central position; and the entire front surface 54 of each of the sheets 52 and 53 can be coated with a release coating 71 (which coating 71 is also not needed if the adhesive is low tack). Like the layers 17 of pressure-sensitive adhesive on the sheets 12 and 13, the layers 57 of pressure-sensitive adhesive on the sheets 52 and 53 are in the form of spaced strips of the adhesive that extend transversely of the sheets parallel to their opposite edges 66 and 67 with each strip being adjacent and extending along an edge of a portion 64 of the sheet that will be formed by separating the sheets 52 and 53 along the paths of weakness 63.

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The sheet assembly 50 also includes indicating means for indicating the orientation of the layers 56 of pressure-sensitive adhesive between the sheets 52 and 53 of the sheet assembly 50. As illustrated that means for indicating the orientation of the layers 56 of pressure-sensitive adhesive is provided in two ways, (1) by end portions of both sheets 52 and 53 adjacent their edges 66 extending past the adjacent edge 67 of the other sheet 52 or 53, and (2) by providing a mark (e.g., an arrow) or indicia (e.g., written instructions) 68 on those projecting portions of the sheets 52 and 53. Alternatively, one of the sheets 12 or 13 could be notched and indicia may be printed on the other sheet in the notch, a projecting portion of one of the sheets 52 or 53 may be used without indicia, or a mark or indicia may be used alone on the front surface 14 and at the edge of either of the sheets 12 or 13, or the sheet assembly may be made without such indicating means.

FIG. 9 illustrates a third embodiment of a sheet assembly 80 according to the present invention that could be used in the methods illustrated in FIGS. 1 and 2, which sheet assembly 80 is essentially the same as the sheet assembly 50 illustrated in FIG. 8 with similar parts being similarly numbered except for the addition of the suffix "a" except that no indicating means is provided, no layers of release coating are provided on the front surfaces of the sheets and no layer of release coating is provided adjacent one of the layers 56a of adhesive adjacent one end of the sheet assembly 80 on the sheet 53a. Thus, one of the sheets 52a of the sheet assembly 80 has a release coating on all of its nonadhesive bearing areas that will be contacted by layers 56a of adhesive and the other sheet 53a of the sheet assembly 80 has a release coating on only a portion of the nonadhesive bearing areas that will be contacted by layers 56a of adhesive so that the adhesion between at least one layer 56a of adhesive and the nonadhesive bearing area it contacts that has no release coating will adhere the sheets 52a and 53a together with sufficient firmness to facilitate printing of the front surfaces 54a of the sheets 52a and 53a without separation of the sheets 52a and 53a.

FIG. 10 illustrates an unfolded sheet assembly 90 comprising two sheets 92 and 93 separated by perforations forming a path of weakness 91 with an alternative pattern to that illustrated in FIGS. 2, 3, 8 and 9 for spaced layers 96 of pressure-sensitive adhesive in a predetermined pattern on rear surfaces 95 of the two sheets 92 and 93. That predetermined pattern is a rectangular pattern with every other rectangle in each direction being the same (i.e., either bearing a layer 96 of pressure-sensitive adhesive or being free of pressure-sensitive adhesive). The layers 96 of pressure-sensitive adhesive in the predetermined pattern on the rear surface 95 of each of the sheets 92 or 93 are adapted to contact and releasably adhere to the rear surface 95 of the other sheet 92 or 93 only in nonadhesive bearing areas of that rear surface 95 that are recessed with respect to the layers 96 of pressure-sensitive adhesive. Also, as illustrated, the sheet assembly 90 has release coatings 100 on the nonadhesive bearing areas of the rear surfaces 95 of the sheets 92 and 93 which are slightly larger in area than the layers 96 of adhesive, and are disposed in a position such that when the rear surfaces 95 of the sheets 92 and 93 are placed face to face while joined along the path of weakness 91, the layers 96 of adhesive will contact and will be generally centered on the release coatings 100. The entire front surface of each of the sheets 92 and 93 may optionally also be coated with a release coating. The illustrated release coatings 100 on the rear surfaces 95 and the release coatings on the front surfaces 94 of the sheets 92 and 93 may not be

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needed when the layers 96 of adhesive are of low-tack or repositionable adhesive, but may be useful if the layers 96 of pressure-sensitive adhesive that are more aggressive or permanent than repositionable adhesive. Pads can be made from the sheet assembly 90 using the method described above with respect to FIGS. 1 and 2 that have one or more of the layers 96 of adhesive adhering together the portions of the sheets 92 and 93 forming the pads. Even when two, four or more of the layers 96 of adhesive adhere together the portions of the sheets 92 and 93 forming the pads, corners of the sheet portions in the pads will be un-adhered to facilitate separation of those corners from the rest of the pad to initiate peeling away of a portion of one of the sheets 92 or 93 in the pad. Such separation may also be facilitated at corners of the pad adjacent the layers of adhesive by removing corners from the otherwise rectangular layers 96 of pressure-sensitive adhesive along the sides of the sheets 92 and 93.

EXAMPLE 1

An example of the sheet assembly 10 illustrated in FIGS. 3 and 4 was made and tested. Release material for the coatings 40 and 41 was prepared in accordance with the teachings in U.S. Pat. No. 5,154,962 (Mertens, et. al.), Example 41, (the content whereof is incorporated herein by reference) except the material was made in 55 gallon reactors, and the chemical composition was 47.0 percent methyl acrylate, 36.5 percent n-vinyl pyrrolidone, 5.3 percent acrylic acid, and 31.3 percent silicone macromer. The dispersion contained 12 percent tetrapolymer, 12 percent butyl carbitol, and 76 percent water. Pressure-sensitive adhesive for the coatings 16 was prepared from the teachings in European Patent Application No. 90313801.4 (Bohnel), Example 21, (the content whereof is incorporated herein by reference) with the material composition being 66.2 percent microsphere dispersion, 27.4 percent Hycar 26222, 19.3 percent deionized water, 0.7 percent ASE 95, 0.1 percent stepanol. A primer for improving the anchorage of the layers 16 of the sheets 12 and 13 web was prepared by dissolving 4.5 parts by weight "Elvanol"™ 71-30 (commercially available from the DuPont Company) into 95.5 parts by weight water. To 69.0 parts by weight of the mixture, was added 35.0 parts by weight 3 micron CaCO₃. The composition was well mixed. The primer was flexographically applied to both sides of the paper sheets 12 and 13, and was dried. The release material and pressure-sensitive adhesive were flexographically printed on and dried on one face of a web of bond paper, to provide the pattern illustrated in FIGS. 3 and 4 with the release coatings 40 in rectangles 20.6 cm wide and 3.8 cm long, and the layers 16 of pressure-sensitive adhesive in rectangles 7.1 cm wide and 3.6 cm long with adjacent aligned layers 16 being separated by 1.0 cm. The web was perforated to provide the paths of weakness illustrated in FIGS. 3 and 4. In subsequent processing, the release coating 41 was coated on the front surfaces 14 of the sheets 12 and 13 using rotogravure processing and was dried. The web was then folded and separated to form sheet assemblies 10 that were 21.6 cm wide by 27.9 cm long, and were perforated in the width every 7.0 cm. Sheet assemblies 10 were then printed in a Hewlett Packard "LaserJet III" on both sides by feeding the assembly through the machine twice. Both graphics and printed indicia were printed on the sheet assemblies 10. Subsequently, the sheets 12 and 13 of the printed sheet assemblies were peeled apart, and torn apart along the perforations or path of weakness 31 at their ends 30. The separated sheets 12 and 13 were then manually

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stacked and separated along the perforations or paths of weakness 33 to provide note pads of the type 42 illustrated in FIG. 5. Similar printed and separated sheets 12 and 13 were manually stacked and separated along the perforations or paths of weakness 33 to provide note pads of the type 44 illustrated in FIG. 6.

EXAMPLE 2

Examples of the sheet assemblies 10 were made using the same bond paper, adhesive, primer, and coating methods and other method described in Example 1, except that the release material used in the coatings 40 on the rear surface 15 was the heat curable silicone, 96 percent "Syl-Off"™ 7676 and 4 percent "Syl-Off"™ 7677 (commercially available from Dow Corning Corp.), and no release coating was applied to the front surface 14 of the sheets 12 and 13. These sheet assemblies were printed and converted into pads in the same manner described in Example 1 and were found to perform well.

EXAMPLE 3

Example sheet assemblies generally of the type 10 illustrated in FIGS. 3 and 4 were made using sheets 12 and 13 of carbonless paper of the type commercially available from 3M under the trademark "Scotchmark". A release material for the coating 40 was prepared by dissolving 12 g "Syl-Off"™ 7610 and 0.5 g "Syl-Off"™ 7611 (both commercially available from Dow Corning (Corp.) into 88 g toluene. An adhesive material for the layers 16 of adhesive was prepared from a suspension in organic solvent of 10 parts of the copolymer of 95% iso-octyl acrylate and 5% acrylic acid and 90 parts of tacky elastomeric copolymer microspheres ranging in diameter from about 10 to 150 micrometers. The adhesive was coated from about 13 percent solids content using a slot with an 0.10 mm orifice to a silicone treated web and dried to form a transfer tape. A swab was prepared to manually apply the release coating in various configurations. The swab used a 3 cm wide paper towel attached to a tongue depressor. Laser pre-perforated carbonless paper was pre-printed and cut to form sheets 21.6 cm wide and 29.2 cm long, each with a perforation 13 mm from the top of the sheet. Two sets of carbonless forms with a top sheet and a second copy sheet were coated with silicone along the terminal edge opposite the perforation. The silicone composition was cured in heat. To both top sheets was applied a 10 mm long strip of transfer tape 20.3 cm wide, along the terminal edge next to the perforation. The silicone web was removed to expose the adhesive. The sheets 12 and 13 were aligned and laminated such that the layer of adhesive 16 on one sheet contacted the release coating of the adjacent sheet. To the bottom sheets was applied a 10 mm long strip of transfer tape 14 cm wide, along the terminal edge next to the perforation. The silicone web was removed to expose the adhesive. The sheets 12 and 13 were aligned and laminated such that the layer of adhesive 16 on one sheet contacted the release coating of the adjacent sheet. The assemblies were found to be stable when handled. Both assemblies were printed in a Hewlett Packard "LaserJet III" laser printer. The assemblies were separated and stacked into two form sets, each with top and bottom sheets. The sets were found to dispense in the manner described by U.S. Pat. No. 5,050, 909.

EXAMPLE 4

An example of the sheet assembly illustrated in FIG. 9 was prepared. Two sheets 52a and 53a of bond paper were

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prepared with dimensions 21.6 cm wide and 14.0 cm long. A transverse perforation 63a was made at 7.0 cm of length for each sheet 52a and 53a. A 20 mm wide swab was prepared as in Example 3. A transfer tape was prepared using the adhesive composition described in Example 3, only it was coated using a 0.05 mm orifice. The adhesive was dried. The silicone from Example 3 was applied to form the coatings 70a in strips across the width of the paper sheets 52a and 53a. Two strips 70a were applied to the first sheet 52a, one along a terminal edge, and the second along the perforation 63a on its side opposite that terminal edge. One strip 70a was applied to the second sheet along the perforation 63a. Two strips of 12 mm long transfer tape were applied across the width of each sheet 52a and 53a to form the layers 56a of adhesive disposed as illustrated in FIG. 9. After the tape was laminated to the sheets 52a and 53a, the release liner was removed to uncover the adhesive. The rear surfaces 55a of the sheets 52a and 53a were adhered together resulting in three layers 56a of adhesive contacting release coatings 70a of silicone and one layer 56a of adhesive strip contacting the uncoated inner surface 55a of the sheet 53a as is illustrated in FIG. 9. The sheet assembly 80 was found to be stable, and was printed in a Hewlett Packard "LaserJet III" laser printer.

EXAMPLE 5

Ten example sheet assemblies 10 were prepared as described above in Example 1. Artwork on a pattern sheet was prepared using computer software and a laser printer. The artwork consisted of eight (8) images positioned on the pattern sheet so that it would generally align with the portions 34 of the sheets 12 and 13 defined by the perforations or paths of weakness 33. Two copies of the pattern sheet were printed by the laser printer and used for printing both front surfaces 14 of the sheet assemblies 10 on a Lanier 6272 copier used in duplex mode. The printed sheets 12 and 13 of the sheet assemblies 10 were sequentially peeled apart and separated at the path of weakness 31. The sheets 12 and 13 were stacked into a master stack 26 as illustrated in FIG. 2 using a box lid elevated at one corner as the stacking frame 25 so that sheets were aligned on the stack 26 against the corner of the box lid opposite its elevated corner. The master stack 26 was cut into 16 individual note stacks 10.8 cm wide and 7.0 cm tall using a guillotine cutter 28.

EXAMPLE 6

Examples of the sheet assembly 90 illustrated in FIG. 10 were made using the materials and processes described in Example 1. The sheet assemblies 90 made were 21.6 cm wide and 27.9 cm long. The layers 96 of adhesive were each about 4.1 cm wide and 2.5 cm long. The sheet assemblies 90 were printed using the artwork illustrated in FIG. 7 using a Lanier 6272 copier in duplex mode. The sheets 92 and 93 of the printed sheet assemblies 90 were separated and stacked as illustrated in FIG. 2 with the layers 96 of adhesive on the sheets 92 and 93 adjacent the front surfaces 94 of the adjacent sheet by aligning corners of the separated sheets 92 and 93 in the corner of a tray, which tray was elevated on its side diagonally opposite the corner against which the sheets were aligned to provide a gravitational aid in alignment. The master stack of the sheets 92 and 93 thus formed was then cut along cut lines 110 illustrated in FIG. 7 to form pads of different sizes. The portions of the sheets 92 and 93 in each pad had at least one layer 96 of adhesive to adhere those portions together, and the sheet portions in the larger pads

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which had two or more diagonally disposed layers 96 of adhesive which adhered them together.

EXAMPLE 7

Examples were made of sheet assemblies specifically designed to be fed through printers, such as digital printers and office copiers, that print sheets on both surfaces in what is often called "duplex" mode. Such printers, for example, print on both surfaces by printing a series of sheets on one surface, accumulating the sheets in a storage tray, and then automatically feeding the sheets from the storage tray and printing them on their second surfaces. One such printer is a xerographic printer manufactured by Xerox Corporation, Rochester, N.Y., and marketed under the name "Docu-Tech". That printer first feeds sheets sequentially from the top of a stack to its printing mechanism, prints those sheets on one side, accumulates the printed sheets in a storage tray, and then prints the sheets on their second surfaces by feeding them into the printing mechanism from the bottom of the stack in the storage tray. Another such printer is a copier manufactured by Lanier Worldwide, Inc., Atlanta, Ga., that uses mechanical sheet feeders to feed the topmost sheet from both the feed tray and from the tray in which the sheets are accumulated after they are printed on one side. Thus sheet assemblies printed in the types of printers described above are acted upon by two sheet feeders that are each designed to separate a single piece of paper from a stack of sheets. Accordingly, sheet assemblies of the type described in this application must be able to resist separation between their first and second sheets as they are fed by the sheet feeders in such printers, for if even partial separation occurs, the sheet can become misaligned to expose adhesive which can effect proper printing, or may wrinkle or buckle which can cause it to jam in the printer.

A sheet assembly particularly adapted to be printed on both sides in the types of printers described above was made which had the structure illustrated in FIG. 3 except that four instead of two layers 16 of pressure sensitive adhesive were placed in spaced relationship on each sheet 12 and 13. The sheets 12 and 13 were each 20 pound bond paper and were each about eight and one half by 11 inches in size, with the sheet 13 being slightly longer so that it projected about 0.1 inch past the edge 37. The layers 16 of pressure sensitive adhesive were microsphere structured copolymer adhesive described in U.S. Pat. No. 3,691,140 (Silver) dispersed in n-heptane at 8 percent solids. The layers of release coating 40 were crosslinked Syl-Off 7676 coated at 20 percent solids in 2-butanone. The paper was first primed with a vinyl solution containing zinc oxide. The release coating 41 was a polymer described in U.S. Ser. No. 08/040876 Example 1, except the composition was KF2001/MA/MAA/MMA 25/50/20/5 dispersed in 2-butanone to 1.5 percent solids. The adhesive was coated to provide an adhesion comparable to Post-it® notes (i.e., approximated 0.6 N/dm adhesion to glass), in 0.75-inch (1.9 cm) wide stripes 16 extending the full width of the sheets 12 and 13. The opposing strip of release coating 40 was coated with a gravure cylinder to provide 1.25-inch (3.2 cm.) wide stripes extending the full width of the sheets 12 and 13. The materials were coated on a wide web and subsequently converted and folded to form the sheet assemblies 10. These sheet assemblies 10 were printed on each sheet 12 and 13 by sending the sheet assembly 10 twice through a Hewlett-Packard LaserJet III xerographic printer. A one-inch (2.54 cm) wide strip was cut from the printed sheet assembly 10 in a direction perpendicular to the fold between the sheets 12 and 13. The portion

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of the strip formed from one of the sheets 12 or 13 was adhesively bonded to a lower plate attached to a constant-rate-extension device, and the portion of the strip formed from the other sheet 12 or 13 was attached to the load cell of that device. The strip portions were separated at 12 inches per minute (30.5 cm/min.) and the force to separate the strip portions was recorded. The average force required to separate the part of each layer of pressure sensitive adhesive 16 on each strip portion from the opposing strip portion was reported as the "separation force", which for this Example was less than 1 gram per inch.

A second test was performed to determine the sheet stability in a duplex printing operation. One hundred (100) sheet assemblies 10 made as described above were placed in the sheet feeder bin of a Lanier 6540 copier commercially available from Lanier Worldwide, Inc., Atlanta, Ga. The copier was placed in duplex mode, set to print 100 consecutive copies on both sides, and started. The number of times the machine stopped or "jammed" because of the sheet assemblies 10 being printed by the machine was reported as the "jam rate", which of the sheet assemblies 10 described above in this Example was 12 sheets per 100.

The strips of release material 40 on a plurality of the sheet assemblies made as described above were then scraped away using razor blades. When the tests described above were repeated, the separation force of the parts of the stripes of adhesive 16 was about in the range of 20 to 30 grams per inch, and the jam rate of the sheet assemblies 10 was reduced to zero (0) sheets per 100.

EXAMPLE 8

Sheet assemblies 10 were made as in Example 7 with a change in the material and coating weight of the release coating 40. The Syl-Off silicone was replaced with a 20 percent solids solution of the release coating described in U.S. Ser. No. 08/040876 Example 1, except the composition was KF2001/MA/MAA/MMA 25/50/20/5 dispersed in 2-butanone. All the strips of release coating 40 were coated at the same coating weight except for the strip of release coating 40 furthest from the fold between the sheets 12 and 13 which was given a heavier coating of the release material. The materials were all coated on a wide web and subsequently converted into the sheet assemblies 10. These sheet assemblies were tested as described in Example 7 resulting in a separation force for the part of the stripe of adhesive 16 furthest from fold being about 7 grams per inch, the separation force of all other parts of the stripes of adhesive 16 being about 72 grams per inch, and the jam rate of the sheet assemblies 10 being zero (0) sheets per 100.

Subsequently, the sheets 12 and 13 of the sheet assemblies 10 were separated and stacked into pads. The process of separating the sheets 12 and 13 induced a curl in the sheets 12 and 13 which was evident in the finished pad, thereby negatively affecting its appearance.

EXAMPLE 9

Sheet assemblies 10 were made as described in Example 8 except the stripes of release material 40 were applied at a heavier coating weight, with the strip of release material furthest from the fold having even a heavier coating weight than the rest. Those sheet assemblies were tested as described in Example 7 resulting in a separation force for the part of the stripe of adhesive 16 furthest from fold being 4 grams per inch, the separation force of all other parts of the stripes of adhesive 16 being 9 grams per

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inch, and the jam rate of the sheet assemblies 10 being zero (0) sheets per 100.

Subsequently, the sheets 12 and 13 of the sheet assemblies 10 were separated and stacked into pads. The process of separating the sheets 12 and 13 did not induce a significant curl in the sheets 12 and 13 so that the finished pads had an acceptable appearance.

From Examples 7, 8 and 9 described above it was determined that in sheet assemblies 10 of the type described in those examples intended to be used in printers that print on both of the sheets 12 and 13 the separation force for the stripes of adhesive 16 (except for the stripe of adhesive 16 furthest from the fold) should be over 5 grams per inch, and should preferably be about in the range of from 9 to 30 grams per inch to produce an acceptable jam rate for such printers.

Also, it is advantageous to provide a very low bond force between the sheets along at least one edge of the sheet assembly to facilitate separation of the sheets 12 and 13 after printing, either manually or by a separating mechanism. In the sheet assemblies described above in Examples 7, 8 and 9 it was found desirable to have a separation force of less than 10 grams per inch for the stripe of adhesive 16 furthest from the fold.

The present invention has now been described with reference to several embodiments thereof. It will be apparent to those skilled in the art that many changes can be made in the embodiments described without departing from the scope of the present invention. Thus the scope of the present invention should not be limited to the methods and structures described in this application, but only by the methods and structures described by the language of the claims and the equivalents of those methods and structures.

We claim:

1. A method for making custom printed notes, said method comprising the steps of:

providing a sheet assembly comprising first and second sheets each having major front and rear surfaces, and layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of the sheets, the layers of pressure-sensitive adhesive on the rear surface of each of the sheets contacting and being releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas that are recessed with respect to the layers of pressure-sensitive adhesive, the pressure-sensitive adhesive along at least some of said pattern of pressure sensitive adhesive requiring a separation force from the rear major surface of the other sheet of over 5 grams per inch;

printing indicia on the front surfaces of both of the sheets in the sheet assembly using a printer that can print sheet on opposite surfaces;

separating the sheets along predetermined planes normal to and extending across the major surfaces of the sheets to form the custom printed notes.

2. A method for making custom printed note pads, said method comprising the steps:

providing a plurality of sheet assemblies each comprising first and second sheets each having major front and rear surfaces and opposite edges, and layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of said sheets, said layers of pressure-sensitive adhesive on the rear surface of each of said sheets in each of said sheet assemblies contacting and being releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas that

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are recessed with respect to the layers of pressure-sensitive adhesive, and being releasably adherable to the front surfaces of the sheets, the pressure-sensitive adhesive along at least some of said pattern of pressure sensitive adhesive requiring a separation force from the rear major surface of the other sheet of over 5 grams per inch;

printing indicia on the front surfaces of both of the sheets in at least some of the sheet assemblies using a printer that can print a sheet on opposite surfaces;

separating the sheets in the sheet assemblies after said printing step; and

stacking the separated sheets to adhere the layers of pressure-sensitive adhesive on the rear surfaces of the sheets to the front surfaces of the sheets with the layers of adhesive in a predetermined orientation with respect to each other.

3. A method for making custom printed note pads according to claim 2 wherein said method further includes the step of separating the stacked sheets along predetermined planes normal to and extending across the major surfaces of the stacked sheets to form the custom printed note pads.

4. A method for making custom printed note pads according to claim 2 wherein said providing step provides the layers of pressure-sensitive adhesive on the rear surfaces of each of said sheets in strips aligned with predetermined ones of the planes along which the stacked sheets are separated in the separating step such that each of the sheet portions in each of the custom printed note pads has a portion of one of the strips of adhesive along a corresponding edge of the pad.

5. A method for making custom printed note pads according to claim 2 wherein said providing step provides the layers of pressure-sensitive adhesive on the rear surfaces of said sheets in strips aligned with the predetermined ones of the planes along which the stacked sheets are separated in the separating step such that each successive sheet portion in each of the custom printed note pads has a portion of one of the strips of adhesive along an opposite edge of the pad.

6. A sheet assembly adapted to be printed on one or both sides and subsequently converted into a plurality of sheets each having printing on one surface and a small area of pressure-sensitive adhesive on an opposite surface, said sheet assembly comprising

first and second sheets each having major front and rear surfaces and opposite edges, and

layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of said sheets,

said pattern of pressure-sensitive adhesive on the rear major surface of each of said sheets contacting and being releasably adhered to the rear major surface of the other sheet only in nonadhesive areas that are recessed with respect to the pattern of pressure-sensitive adhesive, the pressure-sensitive adhesive along at least some of said pattern of pressure sensitive adhesive requiring a separation force from the rear major surface of the other sheet of over 5 grams per inch.

7. A sheet assembly according to claim 6 wherein said adhesive is a low-tack pressure-sensitive adhesive and said nonadhesive bearing areas are free of release coating.

8. A sheet assembly according to claim 7 wherein said low-tack pressure-sensitive adhesive comprises tacky, elastomeric copolymer microspheres.

9. A sheet assembly according to claim 6 further including a release coating on said nonadhesive bearing areas.

10. A sheet assembly according to claim 6 further including a release material on the front surface of one or both of said sheets.

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11. A sheet assembly according to claim 10 wherein said release material comprises an indicia-receptive polymer.

12. A sheet assembly according to claim 6 wherein said sheet assembly further includes means along one of said edges for indicating the orientation of the layers of pressure-sensitive adhesive in the sheet assembly. 5

13. A sheet assembly according to claim 12 wherein a portion of said first sheet adjacent one edge of said first sheet extends past the adjacent edge of said second sheet to provide said means along one of said edges for indicating the orientation of the layers of pressure-sensitive adhesive in the sheet assembly. 10

14. A sheet assembly according to claim 6 wherein said sheets are attached along adjacent edges and have a path of weakness along said joined edges so that the sheets are sufficiently joined together along said edges to facilitate printing of the front surfaces of the sheets without separation of the sheets. 15

15. A sheet assembly according to claim 6 having a release coating on all of the nonadhesive bearing areas of

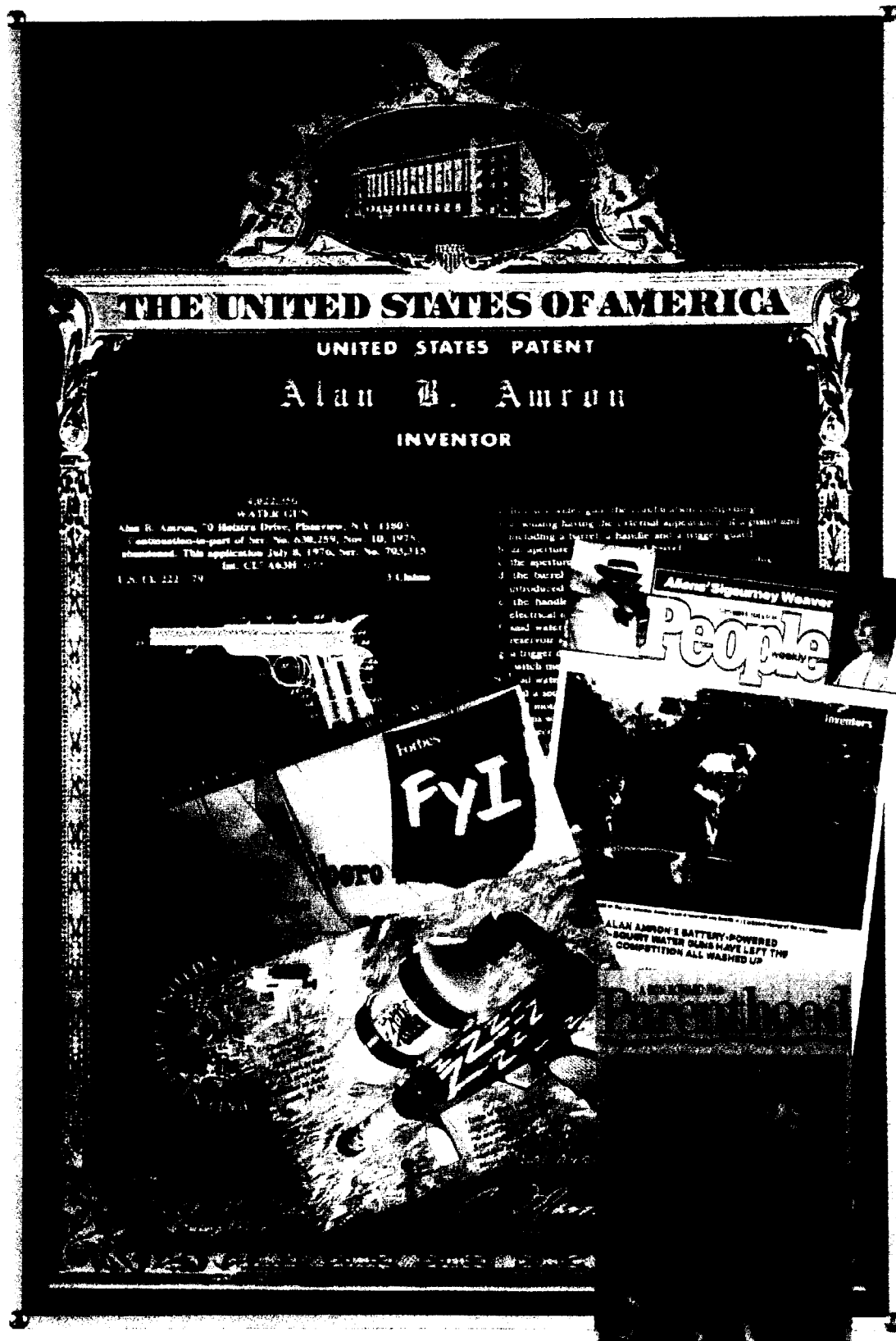
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one of said sheets and having a release coating on only a portion of the nonadhesive bearing areas of the other of said sheets so that the adhesion between at least one layer of adhesive and one nonadhesive bearing area that has no release coating will adhere the sheets together with sufficient firmness to facilitate printing of the front surfaces of the sheets without separation of the sheets.

16. A sheet assembly according to claim 6 wherein said sheets are of material selected from the group consisting of plane paper, bond paper, clay-coated paper, opaque polymeric material, translucent polymeric material and carbonless paper.

17. A sheet assembly according to claim 6 wherein the total area covered by the layers of pressure-sensitive adhesive on both of said sheets is less than 50 percent of the total surface areas of the rear surfaces of both of said sheets.

* * * * *



United States Patent [19][11] **4,022,350**

Amron

[45] **May 10, 1977**[54] **WATER GUN**[76] **Inventor:** Alan B. Amron, 70 Hofstra Drive,
Plainview, N.Y. 11803[22] **Filed:** July 8, 1976[21] **Appl. No.:** 703,315**Related U.S. Application Data**[63] **Continuation-in-part of Ser. No. 630,259, Nov. 10, 1975, abandoned.**[52] **U.S. Cl.** 222/79; 222/333[51] **Int. Cl.²** A63H 3/18[58] **Field of Search** 222/79, 333, 383;
239/332, 587

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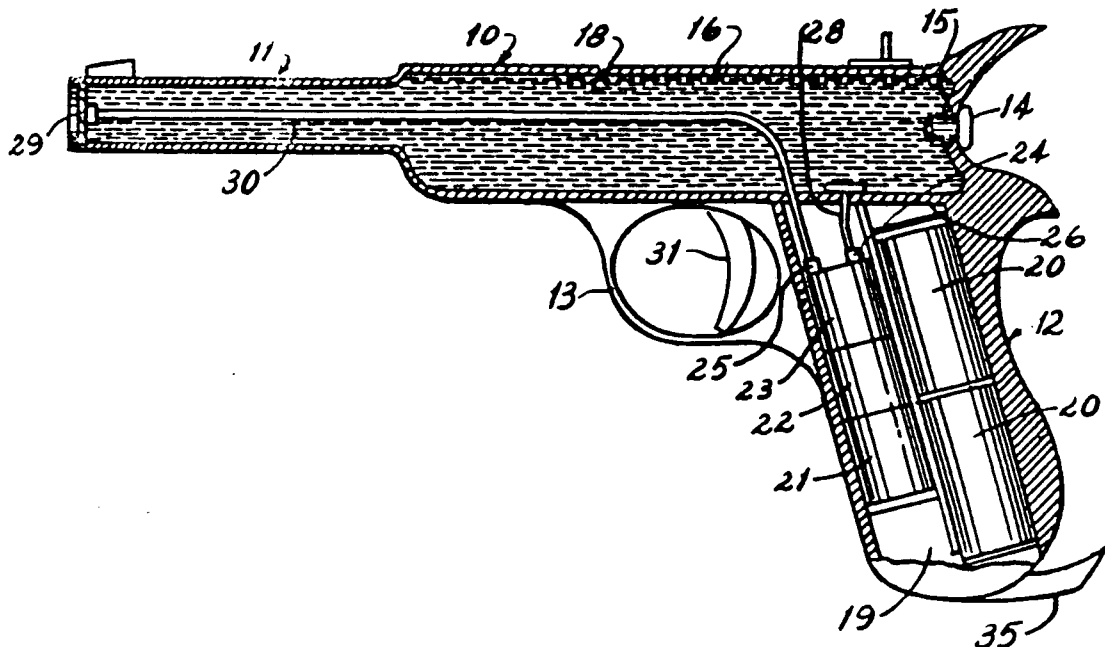
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Primary Examiner—Stanley H. Tollberg
Attorney, Agent, or Firm—Charles Marks

[57]

ABSTRACT

A toy water gun is provided with a battery driven motor and pump assembled with a chamber communicating with a water reservoir and a nozzle in the gun. When the motor and pump are energized, intake and exit valves operate alternately to determine a series of spurts of water from the chamber through the nozzle.

3 Claims, 8 Drawing Figures

U.S. Patent May 10, 1977

Sheet 1 of 3

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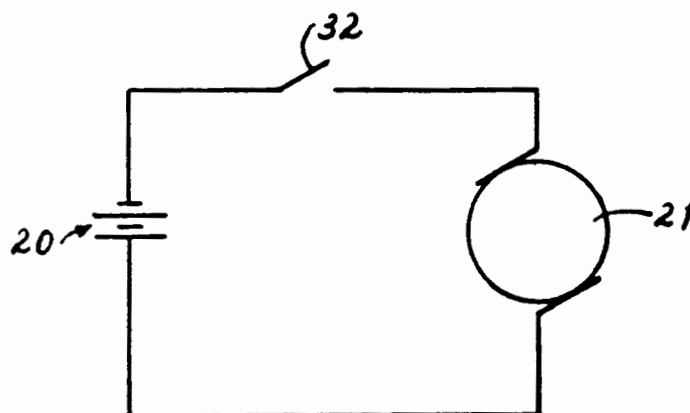
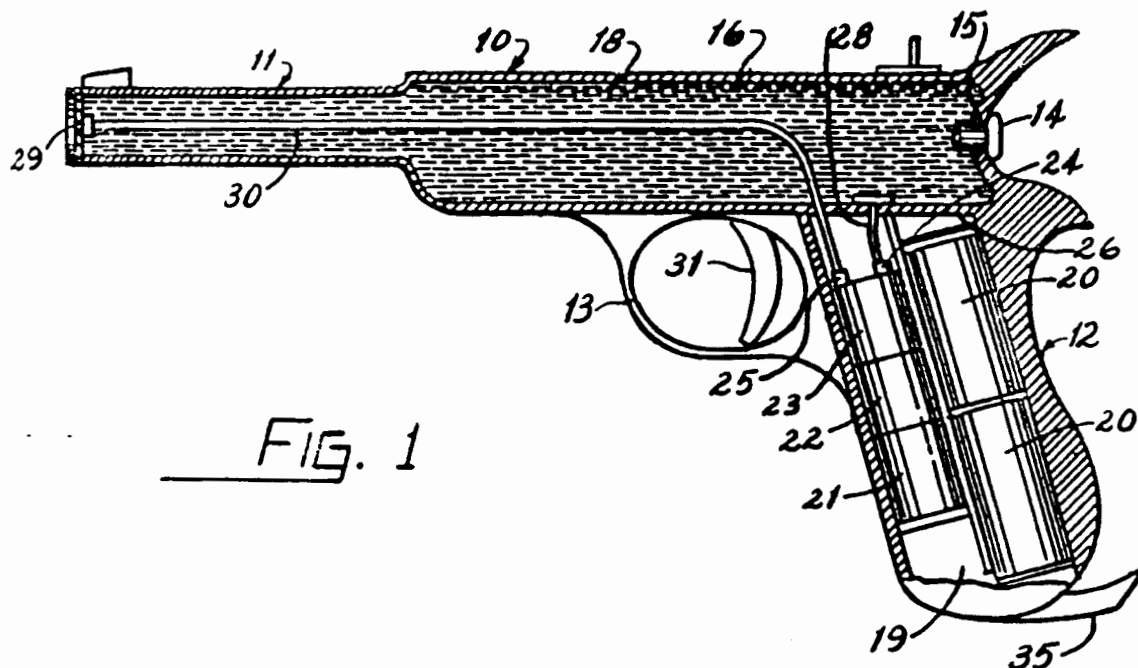


FIG. 3

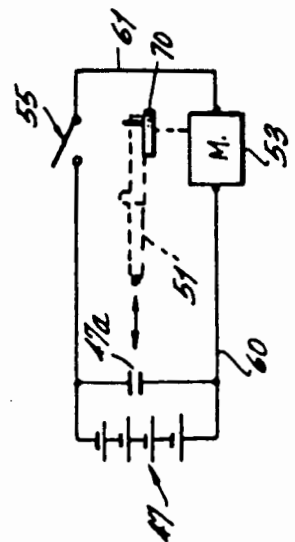
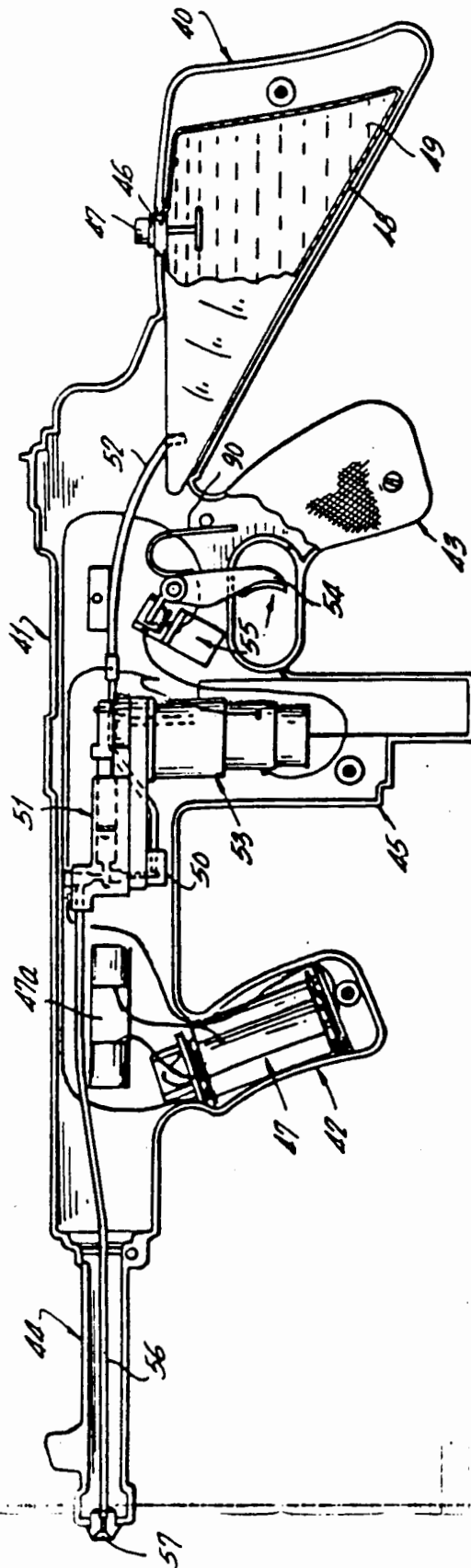


FIG. 4

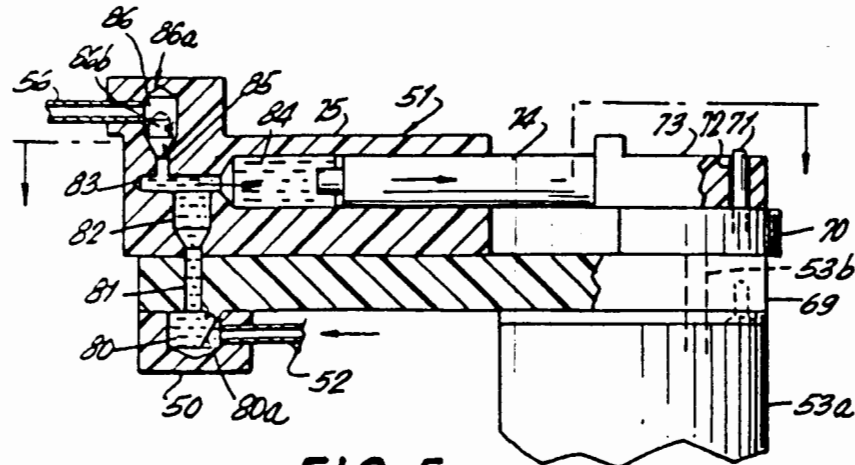


FIG. 5

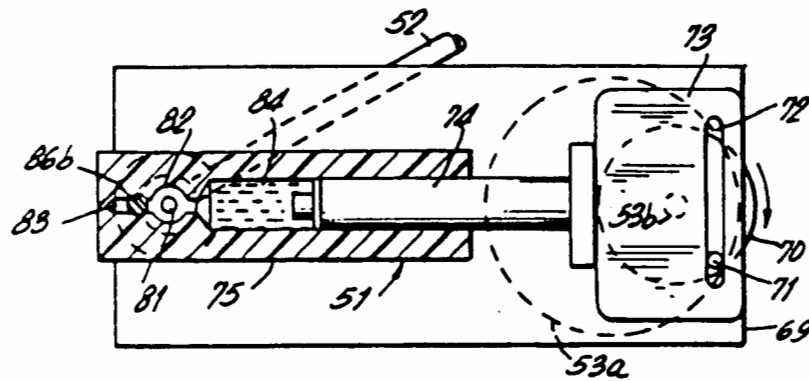


FIG. 6

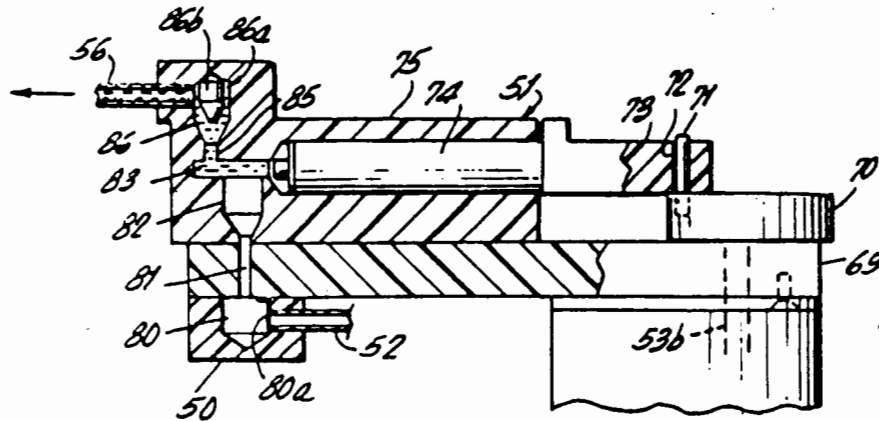


FIG. 7

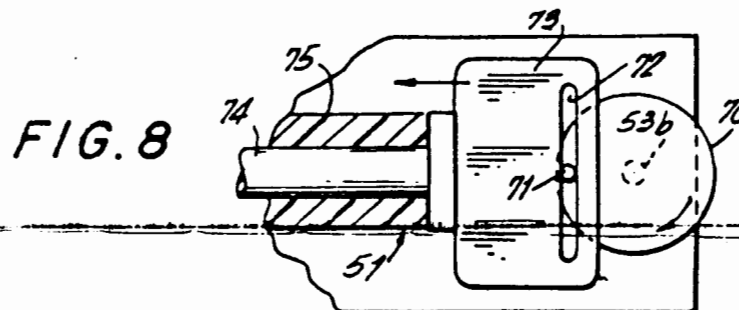


FIG. 8

WATER GUN

BACKGROUND OF THE INVENTION

1. Field of the Invention

This application is a continuation-in-part of application's prior copending application Ser. No. 630,259 filed Nov. 10, 1975 and subsequently abandoned. This invention relates generally to toy water guns and is particularly concerned with electrically operated toy water guns.

2. DESCRIPTION OF THE PRIOR ART

Conventional toy water guns usually depend for their operation upon a trigger actuated mechanical pumping means and produce a continuous stream of water for a period of time corresponding with the actuation of the trigger and the level of pressure produced. Such guns, however, often rely upon a plurality of trigger actuations to accomplish a series of shots, i.e., spurts of water therefrom and, when operated in this way, quickly tire the user.

The present invention solves these problems. Thus, it is an object of the present invention to provide an improved water gun which can be fired in a series of shots by one actuation of its trigger.

Another object of the invention is to provide such a water gun which is electrically operated and which will maintain a high water pressure over a substantial period of time.

Still another object of the invention is to provide such a water gun which incorporates a simple pump and valve means to accomplish its purposes.

Yet another object of the invention is to provide such a water gun which is of simple, economical and sturdy design.

Other and further objects of the invention will become apparent from the following description when read in conjunction with the accompanying drawing.

SUMMARY OF THE INVENTION

The present invention employs a housing in the form of a conventional pistol but having a reservoir accommodating a predetermined quantity of water. The housing includes a handle having a water-tight compartment accommodating one or more batteries actuated by a trigger whereby a switch may be closed to energize a motor driven pump which is also located in the handle. The pump draws water from the reservoir into a chamber and then discharges the water therefrom through a nozzle in the barrel of the pistol. The intake of the water into the chamber is accomplished through a one-way entry valve and its discharge is accomplished through a pressure operated, one-way exit valve. When the chamber is full, the one-way valve is closed, thereby permitting discharge through the pressure operated one-way exit valve. With such discharge, however, the pressure in the chamber drops, thereby permitting the entry valve to open so as to draw more water into the chamber and thereafter close when the water pressure builds up to a point where the water may be discharged through the exit valve. The resulting series of spurts of water will continue as long as the trigger is actuated and the water supply in the reservoir remains.

In a modified form of the invention, the housing is in the form of a conventional, portable machine gun wherein the stock includes a water tight compartment communicating with a battery operated motor and pump assembly and valves in the vicinity of the handles

of the gun to accomplish a series of spurts of water from the barrel thereof in the general manner previously described.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a cross-sectional, diagrammatic view of one embodiment of the invention;

FIG. 2 is a circuit diagram of the electrical system employed in such embodiment of the invention;

FIG. 3 is a modified form of the invention arranged as a machine gun;

FIG. 4 is a circuit diagram of the electrical system employed in said modified form of the invention;

FIG. 5 is a fragmentary, cross-sectional view of the valve system employed in said modified form of the invention;

FIG. 6 is a view taken about the line 6—6 of FIG. 5;

FIG. 7 is another fragmentary, cross-sectional view of the valve system employed in said modified form of the invention;

FIG. 8 is a view taken about the line 8—8 of FIG. 7.

Throughout the various views, similar numerals are employed to refer to similar parts of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in FIG. 1 of the accompanying drawing, one embodiment of the present invention comprises a housing, generally designated by the numeral 10, having the external appearance of a pistol. The housing 10, includes a barrel 11, a handle 12 and a trigger guard 13. The barrel 11 is provided with a removable plug 14 engaged with an aperture 15 communicating with a reservoir 16 in the barrel 11 wherein a quantity of water 18 may be accommodated.

The handle 12 comprises a first chamber 19 accommodating energizing means such as one or more electrical batteries 20. Chamber 19 also accommodates a motor 21, a pump 22 and a second chamber 23 having a one-way intake valve 24 and a one-way exit valve 25. Chamber 19 is sealed against leakage from the reservoir 16 by a partition 26.

The intake valve 24 communicates with the reservoir 16 by means of a drain tube 28 which extends through the partition 26. The exit valve 25 communicates with a nozzle 29 by means of an exhaust tube 30 which also extends through the partition 26, the said nozzle 29 being seated in the mouth of the barrel 11.

A trigger 31 is provided within the trigger guard 13 and functions as a single pole single throw switch (not shown in FIG. 1) which is indicated diagrammatically by the numeral 32 in FIG. 2. When the trigger 31 is pulled, the switch 32 is closed, thereby permitting the batteries 20 to energize the motor 21 and actuate the pump 22. The electrical circuit involved is depicted in FIG. 2. Upon actuation of the pump 22, water is drawn from the reservoir 16 through the drain tube 28 and intake valve 24 into the chamber 23 where it is accumulated and then discharged through exit valve 25, exhaust tube 30 and nozzle 29.

An important feature of the invention resides in the fact that the water is discharged from the nozzle 29 in a series of spurts. This is accomplished by having the intake valve 24 and exit valve 25 permit alternate flow of water therethrough, such mode of operation being accomplished by means well known in the art. For example, the intake valve 24 may be in the form of a

one-way valve and the exit valve 25 may be in the form of a spring-biased poppet valve. Thus, upon the operation of the pump 22, water may be drawn through the intake valve 24 until the chamber 23 is filled, during which time the exit valve 25 remains closed. Thereafter, upon continued operation of the pump 22, the water pressure within the chamber 19 increases so as to close the intake valve 24 and open the exit valve 25, thereby permitting discharge of a quantity of water until the pressure within the chamber 23 decreases so as to permit opening of the intake valve 24 and closing of the exit valve 25. Since the motor 21 operates at high speed and the pump 22 is geared down to permit a correspondingly substantial power, it will be seen that the spurts of water thus produced will emerge from the nozzle 29 with great rapidity, thereby simulating a series of "shots" from the pistol which will continue during the actuation of the trigger 31.

The foregoing description of the operation of the intake and exhaust valves of the chamber 23 is intended to be illustrative only. It is to be understood that other means, such as piston-operation may also be employed to accomplish similar results, such operation including intake and exhaust strokes of the piston in the chamber 23 so as to provide a series of spurts of water from the chamber 23 through the nozzle 29. This mode of operation may be more clearly understood from a consideration of the subsequently described modified form of the invention.

A closure member 35 is hingeably secured to the handle 12 so as to permit access to its interior when desired.

A modified form of the invention is depicted in FIG. 3 through 8. As may be seen in FIG. 3, this form of the invention has the external conformation of a machine gun and includes a shoulder stock 40, a body portion, generally designated by the numeral 41, front and rear handles, generally designated by the numerals 42, 43, a trigger, generally designated by the numeral 44, and an ammunition clip receptacle, generally designated by the numeral 45.

The shoulder stock 40 is provided with an aperture 46 accommodating a removable plug 47 communicating with a reservoir 48 within the shoulder stock 40, said reservoir 48 accommodating a quantity of water 49. The reservoir 48 communicates with a housing 50 of a valve and pump assembly, generally designated by the numeral 51, disposed within the body portion 41, said communication being by means of a tube 52 connected to said reservoir 48 and said housing 50. The valve and pump assembly 51 surmounts a cam and motor assembly, generally designated by the numeral 53, located within the ammunition clip receptacle 45 and energized by a suitable source of electricity such as batteries 47, disposed within the front handle 42 and actuated by a trigger 54 and switch 55.

As hereafter indicated, when the cam and motor assembly 53 is energized, water is drawn from the reservoir 48 through the tube 52 into the valve and pump assembly 51, whence it is discharged through tube 56 and nozzle 57 in the barrel 54, such discharge being intermittent or in spurts of water.

The electrical system involved is depicted diagrammatically in FIG. 4 and is similar to the electrical system used in the first described embodiment of the invention. As indicated in FIG. 4, the electrical system includes the previously mentioned cam and motor assembly 53, batteries 47, a condenser 47a connected in

parallel with the batteries 47, a switch 55, and conductors 60, 61, 62, the cam and motor assembly 53 being surmounted by the valve and pump assembly 51 depicted in broken lines.

The operation of the valve and pump assembly 51 may be better understood from a consideration of FIGS. 5, 6, 7 and 8. As may be seen in FIGS. 5 and 6, the motor 53a is provided with a shaft 53b extending through a plate 69 and connected to a circular cam 70 having an upright eccentric pin 71 slidably engaged with a slot 72 formed in a base plate 73 engaged with a reciprocable piston 74. The piston 74 is accommodated within a cylinder 75 in the valve and pump assembly 51. The aforementioned tube 52 communicates with an intake valve 80 within the housing 50, the said valve 80 being surmounted by an aperture 81 formed in the plate 69 and communicating between said valve 80 and a chamber 82. Valve 80 is provided with a one-way valve gate 80a. Said chamber 82 also communicates with a duct 83 extending from the interior 84 of the cylinder 75. The duct 83 also communicates through channel 85 with the chamber 86 of exit valve, generally designated by the numeral 86a and having a poppet member 86b. Chamber 86 communicates with the aforementioned tube 56.

It will be seen that when the switch 55 is closed by the trigger 54 so as to activate the motor 53a, the cam 70 is rotated, thereby causing the pin 71 to reciprocate the piston 74 within the cylinder 75 and alternately draw water from the reservoir 48 into the interior 84 of the cylinder 75 and discharge it through the tube 56 and nozzle 57 of the barrel 44. As shown in FIGS. 5 and 6, the piston 74 is disposed at the end of its intake stroke whereby water is drawn through tube 52, intake valve 80, chamber 82 and into the interior 84 of cylinder 75. Thereafter, with further rotation of the cam 70, as depicted in FIGS. 7 and 8, the piston 74 accomplishes its exhaust stroke whereby it is moved to the opposite end of the cylinder 75 so as to discharge the water in the interior 84 of the cylinder 75 through duct 83, channel 85, exit valve 86a and tube 56 connected to the nozzle 57 depicted in FIG. 3. During this exhaust stroke, valve gate 80a blocks return of the water to the reservoir depicted in FIG. 3. It is to be understood that valves 80 and 86b may comprise any of a variety of one-way or poppet valves of conventional design. Upon further rotation of the motor the piston 74 performs its intake stroke whereby it is returned to the position depicted in FIGS. 5 and 6 and is ready to begin its above described exhaust stroke again.

Thus, it will be seen that by means of this reciprocating movement of the piston 74, water is alternately drawn from the reservoir 48 and discharged through the nozzle 57, such discharge being interrupted by the said intake strokes so that the discharge is accomplished intermittently or in spurts rather than in a continuous stream.

It will also be observed that this effect is achieved during continuous pull of the trigger 54 whereby the switch 55 is closed, and does not require repeated or a series of pulls of the trigger 54. The trigger 54 is biased by a spring 90, so that when released, the trigger 54 opens the switch 55 and thereby terminates the intermittent discharge of water from the nozzle 57.

I claim:

1. In a toy water gun, the combination comprising:

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- a. a housing having the external appearance of a pistol and including a barrel, a handle and a trigger guard;
 - b. an aperture formed in said barrel;
 - c. the aperture being provided with a removable plug;
 - d. the barrel including a reservoir accommodating water introduced through said aperture;
 - e. the handle including a first chamber accommodating electrical means and water distribution means;
 - f. said water distribution means communicating with said reservoir and a nozzle provided in the barrel;
 - g. a trigger disposed within said trigger guard and including switch means;
 - h. said water distribution means including a motor, a pump and a second chamber;
 - i. said motor and pump being energized by said electrical means when said switch means is actuated by said trigger;
 - j. said second chamber being provided with intake and exit valves operating in sequence, whereby a series of spurts of water is drawn from the reservoir through the intake valve into the second chamber and dispensed therefrom through the exit valve and said nozzle when said motor and pump are energized;
 - k. said handle being provided with closure means.
2. In a device according to claim 1, a water-tight partition between said reservoir and said first chamber.
3. In a toy water gun having the external conformation of a machine gun including a shoulder stock, body

- portion, front and rear handles, a barrel and an ammunition clip receptacle, the combination comprising:
 - a. reservoir formed within said shoulder stock and adapted to accommodate a quantity of water;
 - b. an aperture formed in said shoulder stock and communicating with said reservoir;
 - c. a removable plug accommodated within said aperture;
 - d. reciprocable pump and valve means disposed within said body portion;
 - e. tubular means communicating between said reservoir and said reciprocable pump and poppet valve means;
 - f. tubular means communicating between said reciprocable pump and poppet valve means and a nozzle formed in said barrel.
 - g. electric battery means disposed within one of said handles;
 - h. a motor and cam assembly communicating with a reciprocable piston in said reciprocable pump and poppet valve means;
 - i. a spring-biased trigger disposed within said body portion and communicating with a switch;
 - j. said motor and cam assembly being energized by said electric battery means when said spring-biased trigger actuates said switch, thereby reciprocating said piston and drawing water from said reservoir through said poppet valve means and discharging it intermittently through said nozzle;
 - k. one-way valve means disposed between said reciprocable pump and poppet valve means and said reservoir.

* * * * *

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Nothin' But
on front pag

r power tee ball on Regie



Python add
Toys R Us

Shout N' Shoot on Regis



First ever
Battery operated water gun
prototype!



LARAMI



EMPIRE



BLUE BOX TOY



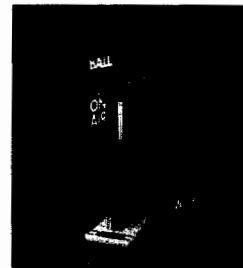
MATTEL/ARCO



TYCO



CAP TOY



LJN



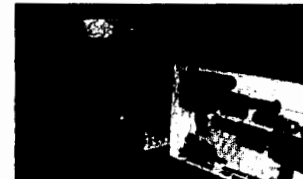
PLAYTIME



CAP TOY



REMCO TOY



THE ORIGINAL TOY MAKERS



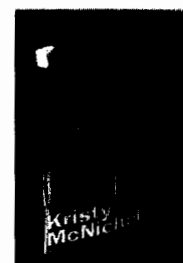
CAP TOY



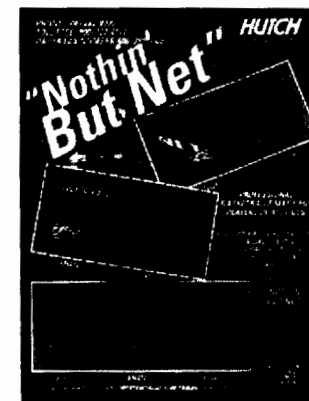
PLAYTIME



PLAYTIME



MEGO TOY



HUTCH/MACGREGOR SPORTS



BEE INTL'



CAP TOY



WRIGLEYS/AMUROL

Alan Amron
77 Horton Place, Syosset, New York 11791

CERTIFIED MAIL #Z-152-277-862
RETURN RECEIPT REQUESTED

October 28, 1997

Mr. Gary L. Griswold, Esq.
Office of Intellectual Property Chief Counsel
Legal Department Building #220-12W-01
3M Center
St. Paul, MN 55144-1000

Dear Mr. Griswold:

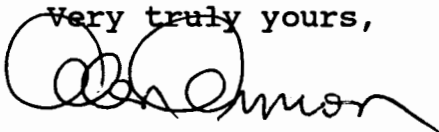
I am Alan Amron. In 1974 I created, invented, offered for sale and put into use a revolutionary new stationary industry product then called "Press on Memo" self stick removeable notes. (This very same product is now made by 3M Commercial Office Supply Division and is sold under the name "Post It Notes.")

My original "Conception Date" and "Offered for sale and put into Public Use date" is July 22, 1974.

I hereby request, by this letter, your permission to manufacturer, license and sell my product worldwide, and or request that you voluntarily withdraw and invalidate, at the United States Patent and Trademark Office in Washington D.C., your patents on same, due to my earlier "Conception Date" and "Offered for Sale and put into public use Date" of July 22, 1974.

I will wait ten (10) business days from the date of this letter for your response.

Very truly yours,

A handwritten signature in black ink, appearing to read 'Alan Amron', with a large circular flourish at the beginning.

Alan Amron

109 PVI

5.45

TOTAL:

5.45

*** U.S. POSTAL SERVICE ***
 SYOSSET POST OFFICE
 SYOSSET NY 11791-9998

CLERK #13

DATE: 10/29/97 12:42:04 PM

109 PVI

5.45

TOTAL:

\$

5.45

*** THANK YOU ***

Z 152 277 862

US Postal Service

Receipt for Certified Mail

No Insurance Coverage Provided.

Do not use for International Mail (See reverse)

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|---|---------|
| Sent to | |
| Intellectual Property Counsel | |
| Street & Number | |
| 3M Center Gary Griswold, Esq. | |
| Post Office, State, & ZIP Code | |
| St. Paul, MN 55144-1000 | |
| Postage | \$ 3.00 |
| Certified Fee | 1.35 |
| Special Delivery Fee | |
| Restricted Delivery Fee | |
| Return Receipt (Providing to Whom) | 1.10 |
| Return Receipt (Showing to Whom, Date, & Addressee's Address) | |
| TOTAL Postage & Fees | \$ 5.45 |
| Postmark Date | |

PS Form 3800, April 1995

USPS 1179

Is your RETURN ADDRESS completed on the reverse side?

SENDER:

- Complete items 1 and/or 2 for additional services.
- Complete items 3, 4a, and 4b.
- Print your name and address on the reverse of this form so that we can return this card to you.
- Attach this form to the front of the mailpiece, or on the back if space does not permit.
- Write "Return Receipt Requested" on the mailpiece below the article number.
- The Return Receipt will show to whom the article was delivered and the date delivered.

I also wish to receive the following services (for an extra fee):

1. ☐ Addressee's Address
2. ☐ Restricted Delivery

Consult postmaster for fee.

3. Article Addressed to:

Mr. Gary L. Griswold, Esq.
 3M Commercial Office Supply Div.
 Office Intellectual Property Counsel
 Legal Dept. Bldg. #220-12W-01
 3M Center
 St. Paul, MN 55144-1000

4a. Article Number:

2152277867

4b. Service Type

- ☐ Registered ☒ Certified
☐ Express Mail ☐ Insured
☐ Return Receipt for Merchandise ☐ COD

7. Date of Delivery

5. Received By: (Print Name)

3m

6. Signature: (Addressee or Agent)

X

8. Addressee's Address (Only if requested and fee is paid)

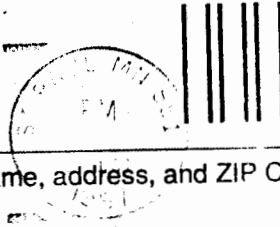
PS Form 3811, December 1994

102595-97-B-0179

Domestic Return Receipt

Thank you for using Return Receipt Service.

UNITED STATES POSTAL SERVICE



First-Class Mail
 Postage & Fees Paid
 USPS
 Permit No. G-10

Print your name, address, and ZIP Code in this box

Alan Amron
 77 Horton Place
 Syosset, New York 11791



AFFIDAVIT

STATE OF FLORIDA :
 :
 : ss.:
COUNTY OF :

I, Jeffrey E. Brown, being duly sworn, deposes and says:

1. I, Jeffrey E. Brown, was a 20% investment partner in the development and sale of the invention for a Press-On Memo pad concept with it's inventor Alan Amron in 1974.

2. I am aware that a New York State Corporation called "Press-On Memo Ltd" had been set up for Mr. Alan Amron's invention in 1974 for the sole purpose of not confusing this invention with any of his other business ventures at that time, and to develop and sell this revolutionary stationary item to retail, wholesale and stationary product manufacturers.

3. I am personally familiar with the purpose of that invention of Mr. Amron's in 1974 called "Press-On Memo Pads". It was, in fact, the first ever memo pads with a sticking glue on the back of each sheet of paper to enable one to post notes in and around the office or home without the use of pins or tape without leaving any residue after removal.

4. I am aware of the Post-It Notes now being sold by the 3M company in stationary stores worldwide and I hereby

confirm that Alan Amron was the first to conceive and first to offer for sale commercially in 1974 a Press-On Memo pad exactly the same as 3M Post-It Notes which were first introduced for sale in and around 1987.

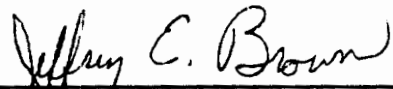
5. My financial investment in Press-On Memo was to be used to fund the cost of developing this invention into a saleable and presentable product, to pay for the printing of the samples, and to do the mass mailing to the stationary industry introducing this item to the world for sale. I felt that my commitment to this novel invention was due to my belief that Press-On Memo pads had huge potential. It appeared to be a revolutionary new stationary item invented by Amron.

6. As I recall, we had joined forces with a sales group called Arkay Sales, Inc. Ronald Katz was the President of Arkay Sales, Inc. and was already established in sales and representation of manufacturers of stationary products. This was a great way for us to tie in our Press-On Memo Pads with the already established stationary industry people.

7. In or around 1987 when 3M Post-It Notes was first introduced into the market place, I had commented to my wife that Alan Amron must have made a business deal with 3M and excluded me from that deal and I was very concerned. I contacted Amron and he assured me that that was not the case,

no deal had been made. It was his intention to locate his original samples and documents of proof first. So that he could then prove beyond any doubt that his conception dates of 1974 for this product were prior to 3M's conception date of 1987. I took him at his word that his intention was to contact me when he had all his evidence gathered. He, in fact, did locate and contact me a few weeks ago.

8. I am without doubt or prejudice that Alan Amron was the originator and creator/inventor of the product that 3 M calls Post-It Notes.



Jeffrey E. Brown

Sworn to before me this
6 th day of June 1997



Notary Public



Darlene M. Sciortino
MY COMMISSION # CC552455 EXPIRES
July 6, 2000
BONDED THROUGH TROY FAIR INSURANCE, INC

AFFIDAVIT

STATE OF NEW YORK)
) SS.:
COUNTY OF NASSAU)

I, MICHAEL SOLOMON, ESQ., being duly sworn, deposes and says:

1. I am an attorney duly admitted to practice in the State of New York and was a partner in the firm of Fritz & Solomon in 1974 with offices located at 33 South Grove Street, Freeport, New York.


2. Alan Amron was a client of our office at that time.

3. Alan had retained our office to file for a New York Corporation called "Press On Memo Ltd". On or about July 24, 1974 we filed the Certificate of Incorporation with the Secretary of State through the office of Gerald Weinberg, Esq., 90 State Street, Albany, New York. A copy of the Certificate of Incorporation is annexed hereto.

4. Alan was a 100% shareholder of the corporation at the time of incorporation.

5. Alan had invented a memo pad with a strip of stickem glue on the back of each sheet of paper enabling one to post notes in and around the office or home without the use of pins or tape and without leaving a glue residue.

6. The purpose of the Corporation was to manufacture and sell press-on memo pads.


MICHAEL SOLOMON

Sworn to before me this
5th day of June, 1997.


Notary Public

ELLEN MAHLAN
Notary Public, State of New York
No. 30-4822673
Qualified in Nassau County
Commission Expires Jan. 31, 1999

A171137 -4

CERTIFICATE OF INCORPORATION
OF
PRESS ON MEMO LTD.

7/23

STATE OF NEW YORK
DEPARTMENT OF STATE
FILED JUL 24 1974
TAX \$
FILING FEE \$

John J. [Signature]

Acting Secretary of State

By *[Signature]*

P. 30/1/1974

Filed by:

Fritz & Solomon, Esqs.
33 South Grove Street
Freeport, New York 11520

1171137

CERTIFICATE OF INCORPORATION
OF
PRESS ON MEMO LTD.

Under Section 402 of the Business Corporation Law.

The undersigned, for the purpose of forming a corporation pursuant to Section 402 of the Business Corporation Law of the State of New York, does hereby certify and set forth:

FIRST: The name of the corporation is PRESS ON MEMO LTD.

SECOND: The purposes, for which the corporation is formed, are:

(1) To print, bind, circulate, distribute, buy, sell, and deal in, books, pamphlets, circulars, posters, newspapers, magazines, literature, music, pictures, tickets, cards, advertisements, letter and bill heads, envelopes, legal, commercial and financial forms and blanks of every kind. To acquire by purchase or otherwise, turn to account, license the use of, assign, and deal with copyrights and intellectual properties of every kind. To carry on a general printing, engraving, lithographing, electrotyping and publishing business in all the branches thereof.

(2) To publish, print and sell newspaper or newspapers, daily, semi-weekly, weekly, or bi-weekly, magazines and periodicals, to print and bind books of all kinds, to do job or general printing and lithographing of all kinds, and generally to do all things that those engaged in a similar business customarily do.

(3) To manufacture, buy, own, sell, import, export, trade and deal in any and all kinds of machinery, apparatus.

appliances, chemicals, metals and materials used for typing, lithographing, photoengraving, photostating, photo-lithographing and similar methods and processes; to manufacture, buy, own, sell, import, export, trade and deal in any and all kinds of printed, electro-plated, electrotyped, lithographed, photo-engraved, photostated, photo-lithographed and similar products, materials, goods and articles, and to perform printing, engraving, electro-plating, electro-typing, lithographing, photo-engraving, photostating, and photo-lithographing operations of every kind and description, and to buy and sell and generally deal in all goods and articles incidental or pertaining to the printing or lithographing business.

(4) To acquire by purchase, subscription, underwriting or otherwise, and to own, hold for investment, or otherwise, and to use, sell, assign, transfer, mortgage, pledge, exchange, or otherwise dispose of real and personal property of every sort and description and wheresoever situated, including shares of stock, bonds, debentures, notes, scrip, securities, evidences of indebtedness, contracts or obligations of any corporation or association, whether domestic or foreign, or of any firm or individual or of the United States or any state, territory or dependency of the United States or any foreign country, or any municipality or local authority within or without the United States, and also to issue in exchange therefor, stocks, bonds or other securities or evidences of indebtedness of this corporation, and, while the owner or holder of any such property, to receive, collect and dispose of the interest, dividends and income on or from such property and to possess and exercise in respect thereto all of the rights, powers and privileges of ownership, including all voting powers thereon.

(5) To construct, build, purchase, lease or otherwise acquire, equip, hold, own, improve, develop, manage, maintain, control, operate, lease, mortgage, create liens upon, sell, convey or otherwise dispose of and turn to account, any and all plants, machinery, works, implements and things or property, real and personal, of every kind and description, incidental to, connected with, or suitable, necessary or convenient for any of the purposes enumerated herein, including all or any part or parts of the properties, assets, business and good will of any persons, firms, associations or corporations.

(6). The powers, rights and privileges provided in this certificate are not to be deemed to be in limitation of similar, other or additional powers, rights and privileges granted or permitted to a corporation by the Business Corporation Law, it being intended that this corporation shall have all the rights, powers and privileges granted or permitted to a corporation by such statute.

THIRD: The office of the corporation is to be located in the Town of Hempstead, County of Nassau, State of New York.

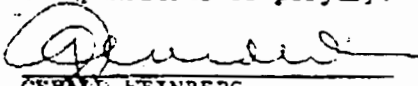
FOURTH: The aggregate number of shares which the corporation shall have the authority to issue is Two Hundred (200), all of which shall be without par value.

FIFTH: The Secretary of State is designated as agent of the corporation upon whom process against it may be served. The post office address to which the Secretary of State shall mail a copy of any process against the corporation served upon him is:

c/o Fritz & Solomon, Esqs.
33 South Grove Street
Freeport, New York 11520

The undersigned incorporator is of the age of twenty one years or over.

IN WITNESS WHEREOF, this certificate has been subscribed to this 22nd day of July, 1974, by the undersigned, who affirms that the statements made herein are true under the penalties of perjury.


GERALD WEINBERG
90 State Street
Albany, New York

CT-4

NEW YORK STATE CORPORATION FRANCHISE TAX REPORT ARTICLE 9A, TAX LAW

(For corporations eligible to file this report, see instruction 1 on Page 2)

1974

CALENDAR YEAR 1974 or other taxable PERIOD

BEGUN _____ 1974 ENDED _____ 19 _____

File with Corporation Tax Bureau, State Campus, Albany, N.Y. 12227, within 2 1/2 months after close of report year. Please read instructions on Page 2 before preparing this report.

PLEASE PRINT OR TYPE

BUREAU USE

EMPLOYER IDENTIFICATION NUMBER

FILE NUMBER

Please use pre-addressed form. Correct any error in Employer Number, address and Zip Code.

NAME

TN 4053 002 8817 241 049.40

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CITY OR TOWN, STATE AND ZIP CODE

CHECK IF CHANGED
SINCE LAST REPORT☐ ADDRESS☐ EMPLOYER NUMBER

342



US005382055A

United States Patent [19]

Mertens et al.

[11] **Patent Number:** 5,382,055[45] **Date of Patent:** Jan. 17, 1995[54] **NOTE OR NOTE PAD PREPARATION METHOD**[75] **Inventors:** Timothy A. Mertens, Cottage Grove; Mark S. Vogel, Maplewood, both of Minn.[73] **Assignee:** Minnesota Mining and Manufacturing Company, St. Paul, Minn.[21] **Appl. No.:** 973,039[22] **Filed:** Nov. 9, 1992[51] **Int. Cl.⁶** B42D 15/00[52] **U.S. Cl.** 283/67; 283/117; 412/1; 412/10; 462/67[58] **Field of Search** 283/67, 117; 412/1, 412/10; 462/67[56] **References Cited****U.S. PATENT DOCUMENTS**

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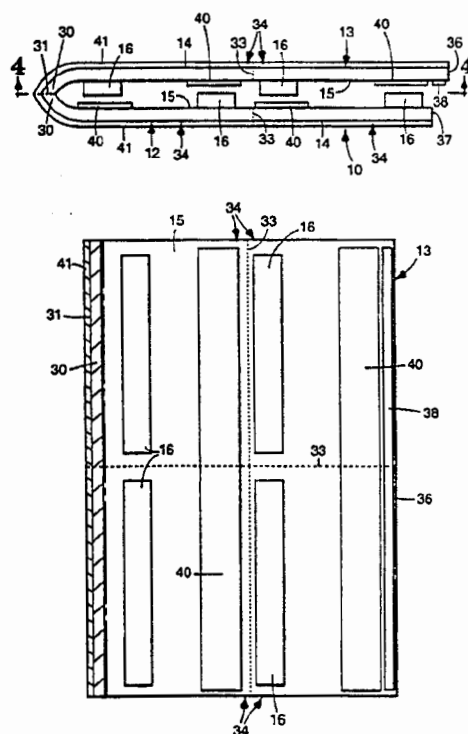
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Primary Examiner—Paul A. Bell*Attorney, Agent, or Firm*—Gary L. Griswold; Walter N. Kirn; William L. Huebsch[57] **ABSTRACT**

A method for making custom printed notes or note pads. One or more sheet assemblies are provided which have first and second sheets and a pattern of pressure-sensitive adhesive on the rear major surface of each of the sheets that contacts and is releasably adhered to the rear major surface of the other sheet only in nonadhesive areas. Indicia is printed on the front major surfaces of the sheets using a conventional copy machine. The sheets can then either be cut along predetermined lines to form the custom printed notes, or the sheets of a plurality of such printed sheet assemblies can be separated, stacked to adhere the patterns of pressure-sensitive adhesive on the rear major surfaces of the sheets to the front major surfaces of the sheets with the edges of the sheets in a predetermined orientation with respect to each other; and the stacked sheets can be cut along predetermined lines to form custom printed note pads.

17 Claims, 6 Drawing Sheets



Jan. 17, 1995

Fig. 1

Fig. 1

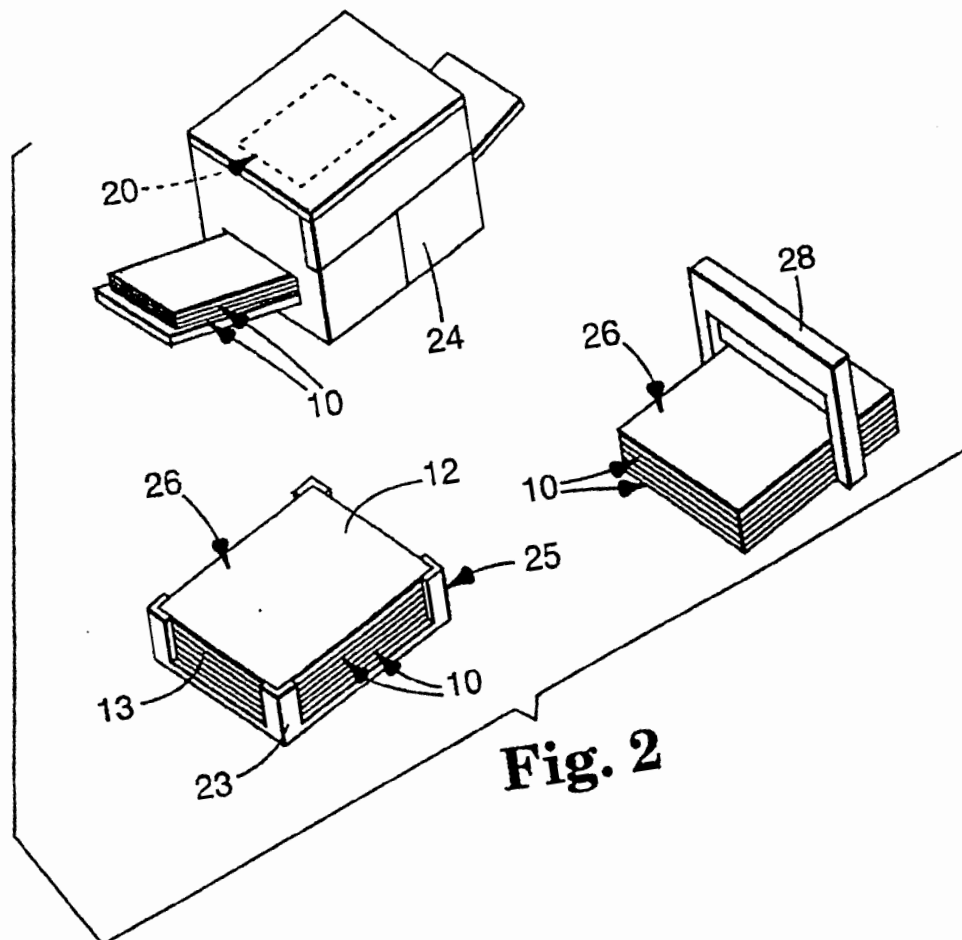
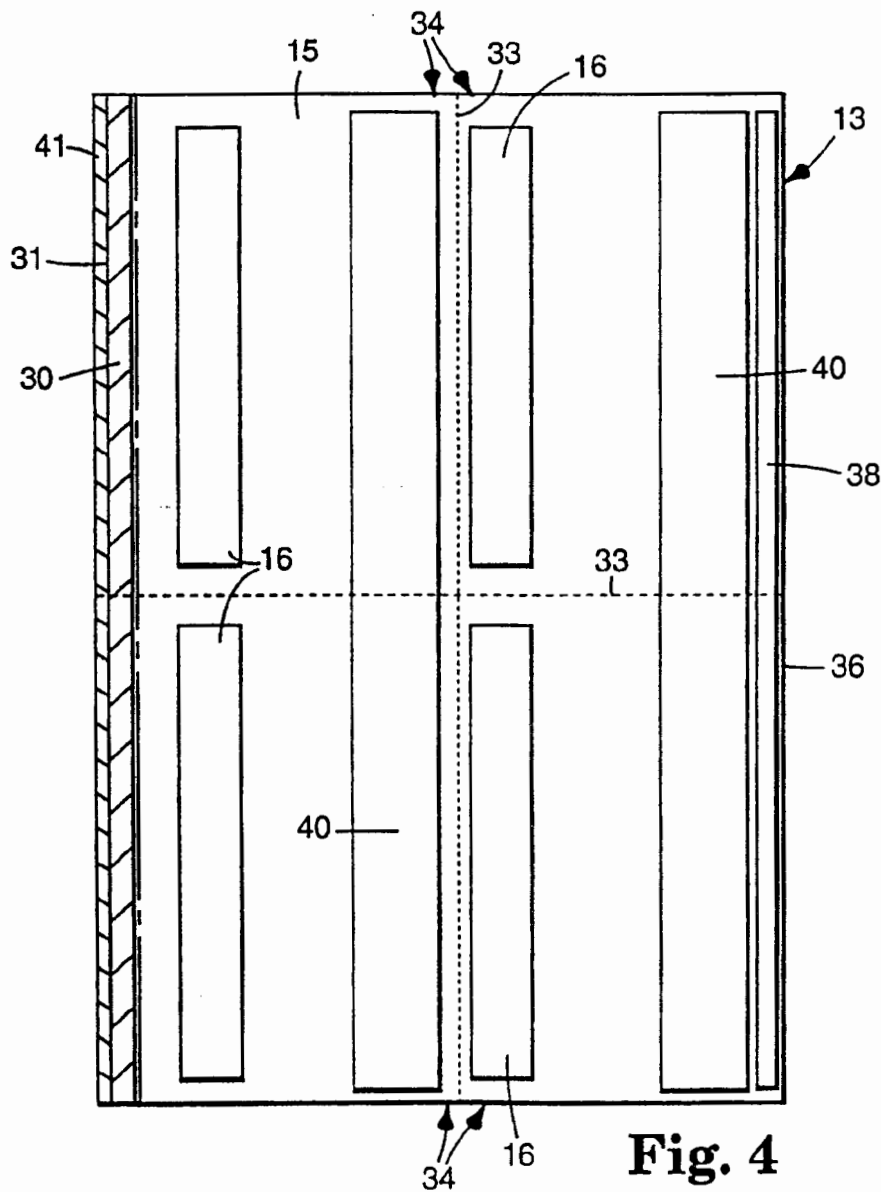
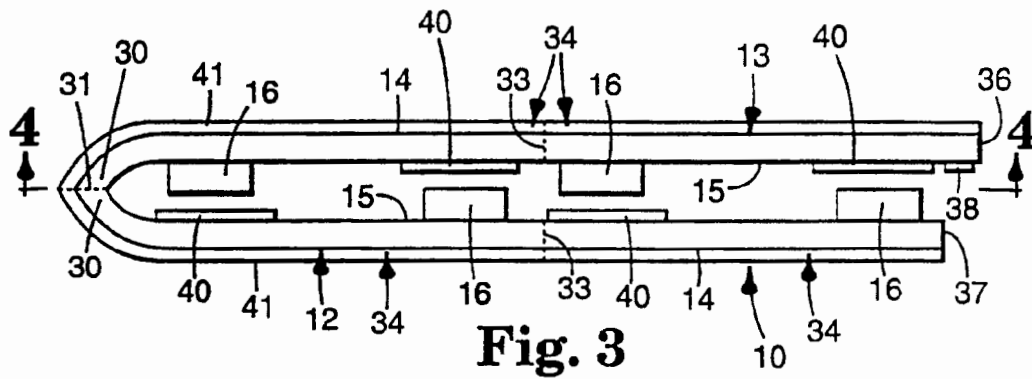


Fig. 2



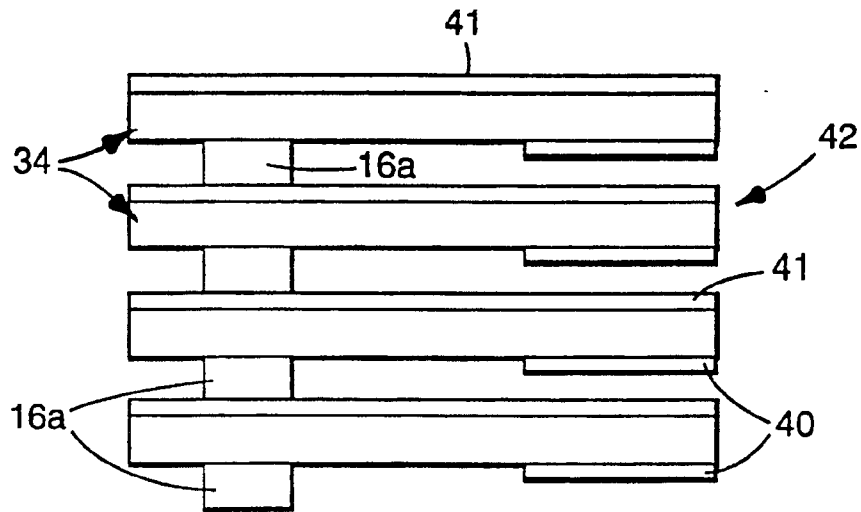


Fig. 5

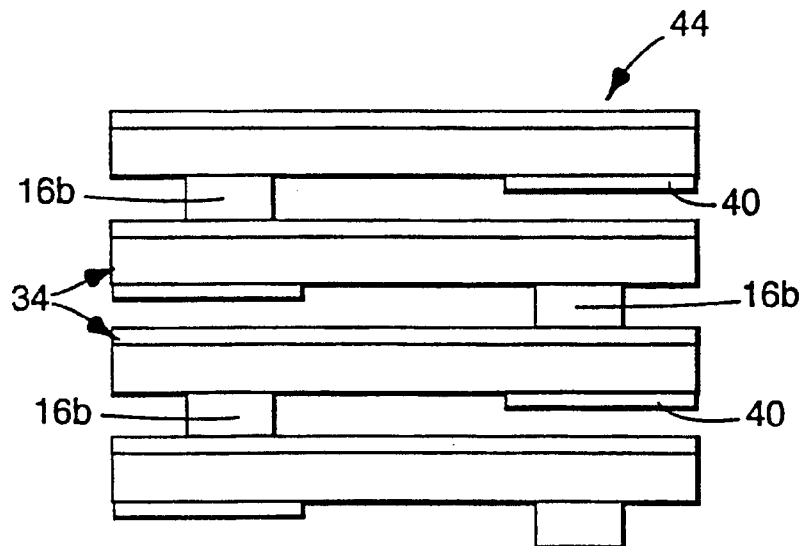


Fig. 6

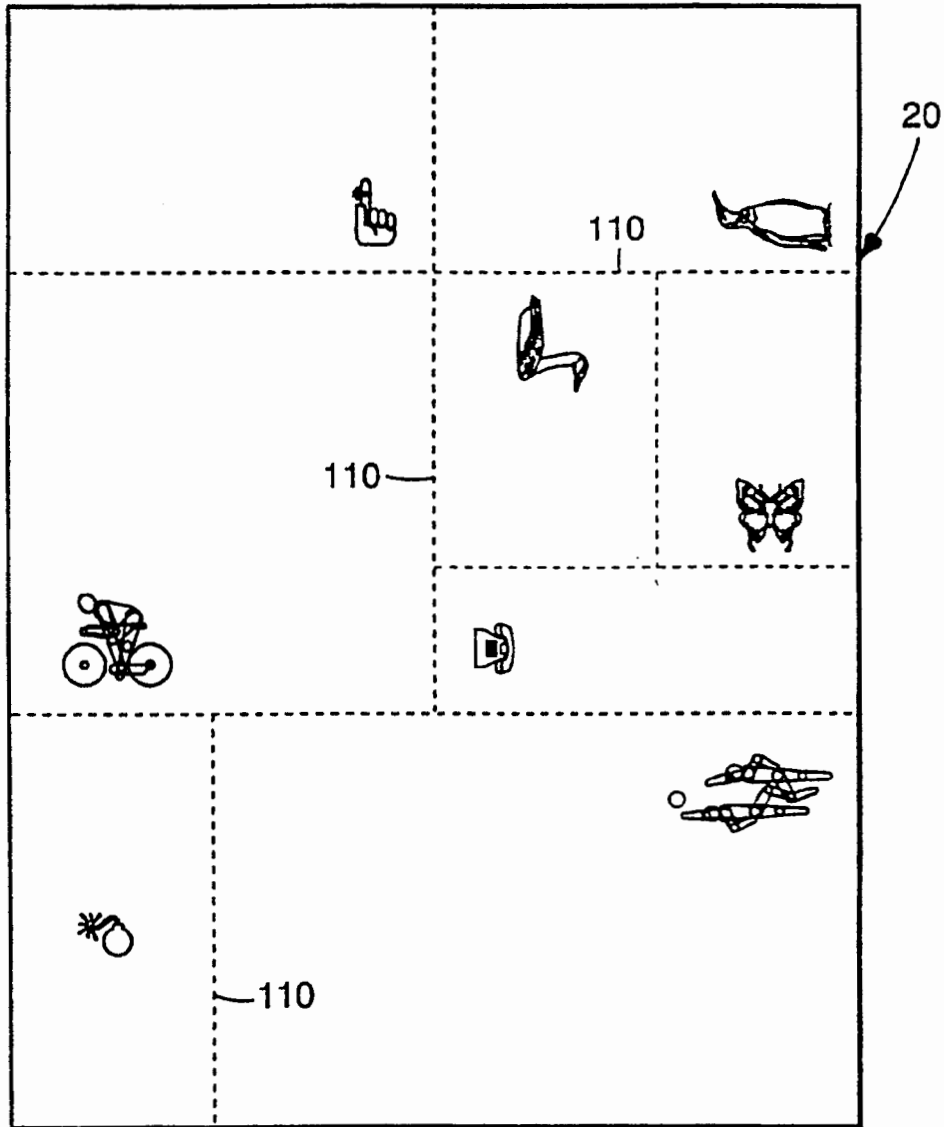
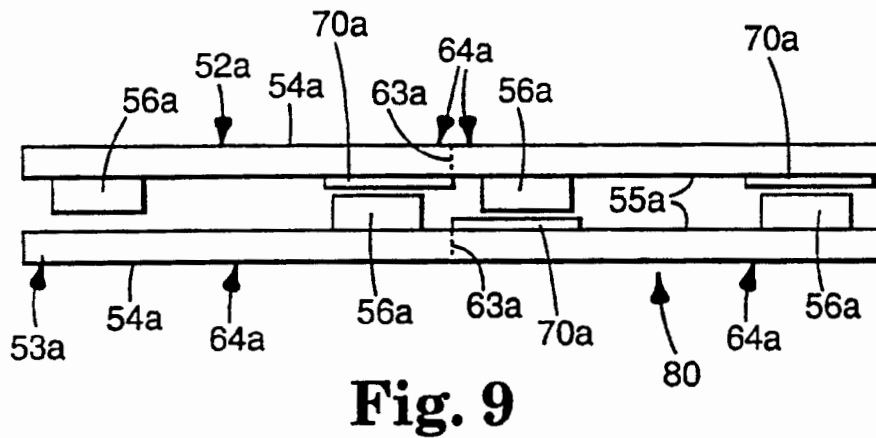
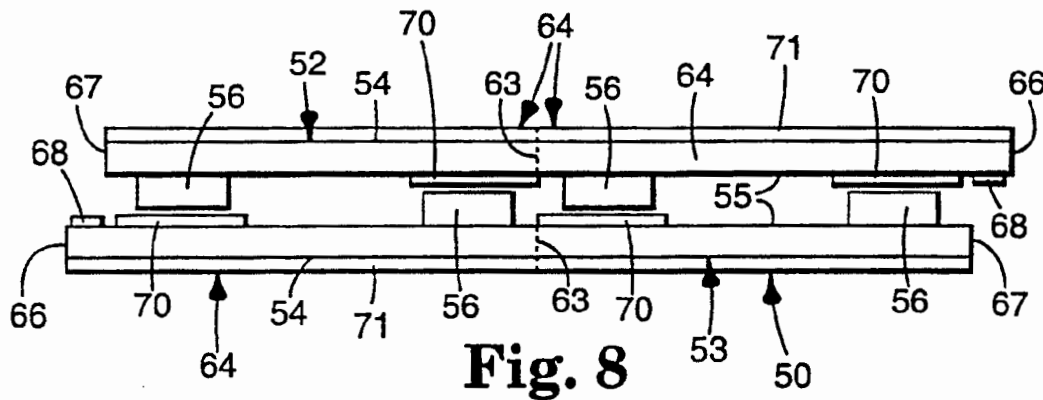


Fig. 7



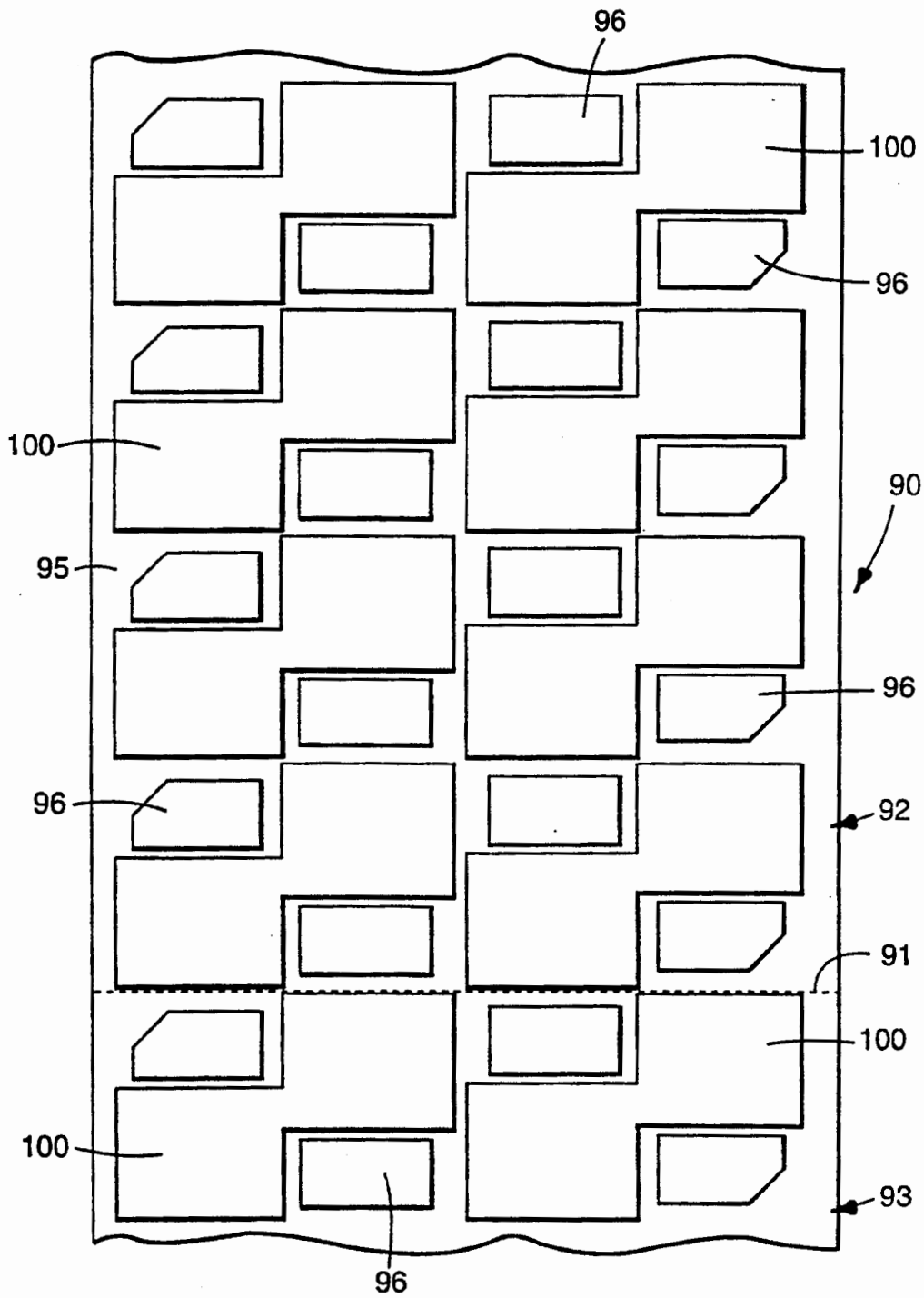


Fig. 10

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NOTE OR NOTE PAD PREPARATION METHOD**TECHNICAL FIELD**

The present invention relates to methods for printing indicia on paper sheets of the type having a narrow strip of pressure-sensitive adhesive adjacent one edge on its rear side by which the sheets can be adhered to a substrate, making pads of such sheets, and to sheet materials used in such printing methods.

BACKGROUND ART

A well known note pad comprises a stack of paper sheets, each having a narrow strip of low-tack pressure-sensitive adhesive adjacent one edge on its rear side by which the sheets can be temporarily adhered to substrates such as documents or other articles (often for message-bearing purposes), by which strip of adhesive the sheets are adhered together in the pad. In one pad configuration, all of the strips of adhesive are along one side of the note pad, whereas in another pad configuration the adhesive strip on each successive sheet in the pad is along the opposite side of the pad as is illustrated in U.S. Pat. No. 4,416,392. Note pads in both of these configurations are currently being marketed under the trademark "Post-it" by Minnesota Mining and Manufacturing Company, St. Paul, Minn. Some such note pads have printed indicia (e.g., a printed message and/or picture and/or decoration) on each sheet, however, heretofore, such indicia has been printed on sheet material from which the note pads are formed by the manufacturer of the note pads, and printing of indicia on such note pads has only been economically feasible when a large amount of such note pads are produced.

DISCLOSURE OF INVENTION

The present invention provides a method, and a sheet assembly used in that method, by which an individual or a small custom printing company can economically prepare a small amount of notes or note pads having pressure-sensitive adhesive on a rear surface and custom printed indicia (e.g., printed messages and/or decorations and/or pictures and/or indicia that make the notes usable as flags, labels or forms) on the front surfaces of all or some of the sheets using conventional printing means including electrophotography through laser printers, conventional office copiers, lithography, flexography, or the like.

The method for making custom printed notes or note pads according to the present invention utilizes one or more novel sheet assemblies, each of which has first and second sheets and layers of pressure-sensitive adhesive in a predetermined pattern on the rear major surface of each of the sheets that contact and are releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas. Indicia are printed on the front major surfaces of the sheets using conventional printing means of the type described above. The sheets can then either be separated along predetermined planes normal to and extending across the major surfaces of the sheets to form the custom printed notes, or the sheets of a plurality of such printed sheet assemblies can be separated, stacked to adhere the layers of pressure-sensitive adhesive on the rear surfaces of the sheets to the front surfaces of other sheets in the stack with the layers of adhesive on the sheets in a predetermined orientation with respect to each other; and the stacked sheets can be separated along predetermined planes

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normal to and extending across the major surfaces of the sheets to form the custom printed note pads.

The adhesive used in the layers of pressure-sensitive adhesive can be a low-tack pressure-sensitive adhesive (e.g., comprising tacky, elastomeric copolymer microspheres) in which case the nonadhesive bearing areas on the rear surfaces of the sheets to which the layers of adhesive are adhered in the sheet assemblies and the front surfaces of the sheets can be free of release coating; or a conventional more aggressive pressure-sensitive adhesive can be used in which case the sheet assembly can include a release coating on those nonadhesive bearing areas to afford separation of the sheets of the sheet assembly after printing, and can further include a release material on the front major surface of one or both of the sheets (e.g., an indicia-receptive polymer) which affords separation of the sheets from the stack.

The sheet assembly can further include orientation indicating means for indicating the orientation of the layers of adhesive on the sheet assembly between the sheets to afford printing in the proper orientation on the sheet, to facilitate separation of the sheets in the sheet assembly, and to facilitate subsequent stacking of the sheets in a desired orientation. The orientation indicating means can be visible, tactile, olfactory, auditory, or tasteable, and can, for examples, be provided by (1) a portion of one sheet adjacent one of its edges extending past the adjacent edge of the other sheet, (2) printed marks on the front surface of one or both of the sheets or printed marks on such a projecting portion, (3) embossed tactile markings on one or both of the sheets, (4) scented portions of one or both of the sheets, (5) coatings on one or both of the sheets that can be tasted, or (6) rough portions on one or both of the sheets that cause a raspy sound when the edge of an object such as a fingernail is rubbed over it. Providing more than one of such orientation means could be useful to accommodate possible users with certain physical handicaps.

The sheets in the sheet assembly can be of any conventional material (e.g., conventional, bond, or clay-coated paper, opaque or translucent polymeric material, or the carbonless paper sold under the trademark "Scotchmark" by Minnesota Mining and Manufacturing Company, St. Paul, Minn. which is paper containing structures such as micro-encapsulated chemicals that will form an image on the paper when pressure is applied to the paper so that, for example, the capsules are broken by the pressure to release the image forming chemical). The sheets in the sheet assembly can be entirely separate and attached only by the layers of adhesive, or can be made from a larger sheet or web in such a way that they are attached along adjacent edges and have a path of weakness along those attached edges. By "Path of weakness" we mean any weakening of the sheet material along a line that permits the sheets to fold or tear apart along that line while providing sufficient integrity so that the sheets do not separate along that line while they are being imprinted. A suitable path of weakness can be provided by forming spaced perforations through the sheet, crushing the sheet, chemical treatment to reduce the thickness and/or the strength of the sheet, grooves formed by control-depth cuts, or the like.

BRIEF DESCRIPTION OF DRAWING

The present invention will be further described with reference to the accompanying drawing wherein like

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reference numerals refer to like parts in the several views, and wherein:

FIG. 1 is a schematic view of a first embodiment of a method according to the present invention for making custom printed notes;

FIG. 2 is a schematic view of a second embodiment of a method according to the present invention for making custom printed note pads;

FIG. 3 is an edge view of a sheet assembly according to the present invention that can be used in the methods illustrated in FIGS. 1 and 2;

FIG. 4 is a reduced sectional view taken approximately along line 4—4 of FIG. 3;

FIGS. 5 and 6 are edge views of optional forms of note pads made by the method of FIG. 2;

FIG. 7 is a plan view of a pattern sheet that can be used in the methods illustrated in FIGS. 1 and 2; and

FIGS. 8 and 9 are edge views of second and third alternate embodiments of sheet assemblies according to the present invention that can be used in the methods illustrated in FIGS. 1 and 2;

FIG. 10 is a fragmentary view illustrating an alternative pattern for layers of adhesive that can be used on a sheet assembly used in the methods illustrated in FIGS. 1 and 2.

DETAILED DESCRIPTION

Referring now to FIG. 1 of the drawing, there is schematically illustrated a first embodiment of a method according to the present invention for making a small amount of custom printed notes. Generally that method comprises the steps of (1) providing a sheet assembly such as the sheet assembly 10 illustrated in FIGS. 3 and 4 which comprises first and second sheets 12 and 13 each having major front and rear surfaces 14 and 15, and spaced layers 16 of pressure-sensitive adhesive in a predetermined pattern on the rear surface 15 of each of the sheets 12 and 13, the layers 16 of pressure-sensitive adhesive in the predetermined pattern on the rear surface 15 of each of the sheets 12 or 13 contacting and releasably adhering to the rear surface 15 of the other sheet 12 or 13 only in nonadhesive bearing areas of that rear surface 15 that are recessed with respect to the layers 16 of pressure-sensitive adhesive (such contact not being illustrated in FIG. 3); (2) printing indicia on at least one of the front surfaces 14 of the sheets 12 and 13 in the sheet assembly 10 using a printing device such as a conventional office copy machine 19 for which there has been prepared an appropriate pattern sheet to be copied, such as the pattern sheet 20 illustrated in FIG. 7; (3) and separating portions of the sheets 12 and 13 along predetermined planes normal to and extending across the major surfaces 14 and 15 of the sheets 12 and 13 to form the custom printed notes (each separated portion having two such notes releasably adhered together by the parts of the layers 16 of adhesive on the notes), which separating could be done by tearing the sheets 12 and 13 along patterns of weakness between the sheet portions (if such patterns of weakness are provided), or by cutting with a conventional scissors, but as illustrated is being done by cutting with a conventional office paper cutter 22. This method allows a person having the sheet assembly 10, a pattern sheet such as the pattern sheet 20 which the person could prepare with custom indicia, and access to a copy machine 19 to easily make a small number of notes having pressure-sensitive adhesive on their back surfaces which are

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printed with indicia of that persons choosing on their front surfaces.

Referring now to FIG. 2 of the drawing, there is schematically illustrated a second embodiment of a method according to the present invention for making custom printed note pads. Generally that method comprises the steps of (1) providing a plurality of sheet assemblies such as the sheet assembly 10 illustrated in FIGS. 3 and 4, each of which sheet assemblies 10 comprises first and second sheets 12 and 13 each having major front and rear surfaces 14 and 15 and layers 16 of pressure-sensitive adhesive in a predetermined pattern on the rear surface 15 of each of the sheets 12 and 13, the layers 16 of pressure-sensitive adhesive on the rear major surface 15 of each of the sheets 12 or 13 in each of the sheet assemblies 10 contacting and being releasably adhered to the rear surface 15 of the other sheet 12 or 13 only in nonadhesive bearing areas that are recessed with respect to the layers 16 of pressure-sensitive adhesive; (2) printing indicia on at least one and usually both of the front surfaces 14 of the sheets 12 and 13 in at least some and usually all of the sheet assemblies 10 (which indicia could be different on different sheet assemblies 10) using a printing device 24 of the type often found in small printing shops (e.g., a conventional office copy machine for which an appropriate printing pattern is provided by a pattern sheet that is copied such as the pattern sheet 20 illustrated in FIG. 7, electrophotography through laser printers for which an appropriate printing pattern is provided by digital electronic signals from a computer or the like, or lithography or flexography for which an appropriate printing pattern is provided by printing plates); (3) separating the sheets 12 and 13 in the sheet assemblies 10 after the printing step (not shown); (4) stacking the separated sheets 12 and 13 (e.g., in a stacking frame 25 which aligns adjacent edges of the sheets 12 and 13 adjacent one lower corner 23 of the frame as illustrated) to adhere the layers 16 of pressure-sensitive adhesive on the rear surfaces 15 of the sheets 12 and 13 to the front surfaces 14 of the other sheets 12 and 13 in the stack to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation with respect to each other; and (5) separating the stacked sheets 12 and 13 along predetermined planes normal to and extending across the major surfaces 14 and 15 of the sheets 12 and 13 in the master stack 26 to form the custom printed note pads; which separating could be done by tearing the sheets 12 and 13 along patterns of weakness between the sheet portions (if such patterns of weakness are provided and the note pads are made using very few sheet assemblies 10), or by cutting with a conventional office paper cutter, but, as illustrated, is being done by cutting with a conventional guillotine cutter 28 of a type often found in small printing companies. This method is particularly useful for persons or companies that provide small printing and copying services to the public (e.g., the companies having the trademark "Insty-prints") so that they can form a small amount of custom printed note pads for customers.

The sheets 12 and 13 of the sheet assembly 10 illustrated in FIGS. 3 and 4 are half portions of a large sheet or web and joined along adjacent edges 30, with a path of weakness 31 provided by spaced perforations along those joined edges 30 so that the sheets 12 and 13 are folded and can be torn apart along that path of weakness 31, while the strength of attachment between the sheets 12 and 13 across that path of weakness 31 pre-

vents the sheets 12 and 13 from separating along their joined edges 30 while they are being printed. Optionally, as illustrated, the sheets 12 and 14 can also be perforated to have additional paths of weakness 33 along planes normal to and extending across the surfaces 14 and 15 of the sheets 12 and 13 so that the sheets 12 and 13 can be manually separated into segments 34. The sheets 12 and 13 have adjacent terminal edges 36 and 37 respectively that are opposite the joined edges 30 and between which separation of the sheets 12 and 13 may be initiated. The layers 17 of pressure-sensitive adhesive on the sheets 12 and 13 are in the form of spaced strips of the adhesive that extend transversely of the sheets 12 and 13 parallel to the edges 30, 36 and 37 with each strip being adjacent and extending along an edge of a portion 34 of the sheet that will be formed by separating the sheets 12 and 13 along the paths of weakness 31 and 33. The sheet assembly 10 is illustrated in FIGS. 3 and 4 with release coatings 40 on the nonadhesive bearing areas of the rear surfaces 15 of the sheets 12 and 13. The release coatings 40 are also in strips, are slightly wider than the strips 16 of adhesive, and extend transversely of the sheets 12 and 13 parallel to the edges 30, 36 and 37 with each strip release coating 40 being adjacent and extending along an edge of a portion 34 of the sheet 12 and 13 that will be formed by separating the sheets 12 and 13 along the paths of weakness 31 and 33, and in a position such that when the rear surfaces 15 of the sheets are placed face to face as illustrated in FIG. 3, the strip layers 16 of adhesive will contact and will be generally centered on the strip release coatings 40. Also, as illustrated, the entire front surface 14 of each of the sheets 12 and 13 is coated with a release coating 41. The illustrated release coatings 40 on the rear surfaces 15 and the release coatings 41 on the front surface 14 of the sheets 12 and 13 are not needed when the layers 16 of adhesive are of low-tack or repositionable adhesive (e.g., the low-tack adhesives based on tacky, elastomeric copolymer microspheres disclosed in U.S. Pat. Nos. 3,691,140 and 3,857,731). The use of the release coatings 40 and 41 allows the use of layers 16 of pressure-sensitive adhesive that are more aggressive or permanent than repositionable adhesive. Suitable release coatings 40 and 41 are materials and treatments which provide a controlled separation force from the layers 16 of adhesive. The release coating 41 should comprise an indicia-receptive material or polymer to facilitate printing on the front surfaces 14 of the sheets 12 and 13. Typical release coatings 40 and 41 include silicones, acrylates, chrome complexes, and fluorochemicals. Even with layers 16 of aggressive pressure-sensitive adhesive the release coatings 40 and 41 might not be required if the sheets 12 and 13 are of a material, or are impregnated with a material, from which the layer 16 of adhesive readily releases.

The sheets 12 and 13 are generally of flat, flexible material including, but not limited to, plain or bond paper, clay coated paper, films, foils, nonwoven materials, opaque or transparent polymeric materials and carbonless paper, and could have double layers so that they form pouches or envelopes.

The sheets 12 and 13 can be stacked as described above to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation directly above each other which can result in note pads such as a note pad 42 illustrated in FIG. 5 which has a portion 16a of one of the layers 16 of adhesive along a corresponding edge of each portion 34 of

one of the sheets 12 or 13 in the pad 42; or the sheets 12 and 13 can be stacked to form a master stack 26 with the layers 16 of adhesive on the sheets 12 and 13 in a predetermined orientation spaced from above each other which can result in note pads such as a note pad 44 illustrated in FIG. 6 in which each successive portion 34 of one of the sheets 12 or 13 in the pad has a portion 16b of one of the layers 16 of adhesive along an opposite edge of the pad 44.

The sheet assembly 10 also includes indicating means for indicating the orientation of the layers 16 of pressure-sensitive adhesive between the sheets 12 and 13 of the sheet assembly 10. As illustrated that indicating means for indicating the orientation of the layers 16 of pressure-sensitive adhesive is provided in two ways, (1) by a portion of the second sheet 13 adjacent its edge 36 extending past the adjacent edge 37 of the first sheet 12, and (2) by providing a mark or indicia 38 on the projecting portion of the second sheet 13. With appropriate instructions (which may be provided by the indicia 38) a user can be made aware of the orientation of the layers 16 of adhesive with respect to the edges of the sheets 12 and 13 in the sheet assembly 10 so that he can print the indicia on the front surfaces 14 of the sheets 12 and 13 in the proper orientation with respect to those layers 16 of adhesive. As an alternative to the indicating means illustrated, either a projecting portion of one of the sheets 12 or 13 or a mark or indicia such as the indicia 38 illustrated may be used alone, or the sheet assembly 10 could be made without any such indicating means.

FIG. 8 illustrates a second embodiment of a sheet assembly 50 according to the present invention that could be used in the methods illustrated in FIGS. 1 and 2. Like the sheet assembly 10 illustrated in FIGS. 3 and 4, the sheet assembly 50 illustrated in FIG. 8 comprises first and second sheets 52 and 53 each having major front and rear surfaces 54 and 55, and spaced layers 56 of pressure-sensitive adhesive in the same predetermined pattern on the rear surface 55 of each of the sheets 52 and 53, the layers 56 of pressure-sensitive adhesive in the predetermined pattern on the rear surface 55 of each of the sheets 52 or 53 contacting and releasably adhering to the rear surface 55 of the other sheet 52 or 53 only in nonadhesive bearing areas 58 of that rear surface 55 that are recessed with respect to the layers 56 of pressure-sensitive adhesive (such contact not being illustrated in FIG. 8). Unlike the sheets 12 and 13 of the sheet assembly 10 illustrated in FIGS. 3 and 4, the sheets 52 and 53 are totally separate rather than being joined along one edge, and each of the sheets has corresponding opposite edges 66 and 67. Optionally, as illustrated and like the sheets 12 and 13, the sheets 52 and 53 can also be perforated to have paths of weakness 63 along planes normal to and extending across the surfaces 54 and 55 of the sheets 52 and 53 so that the sheets 52 and 53 can be manually separated into segments 64; and the sheet assembly 50 can have release coatings 70 on the nonadhesive bearing areas of the rear surfaces 55 of the sheets 52 and 53 (which coatings 70 are not needed if the adhesive is low tack) which coatings 70 are also in strips, are slightly wider than the strips 56 of adhesive, and extend transversely of the sheets 52 and 53 parallel to the edges 66 and 67 with each strip release coating 70 being adjacent and extending along an edge of a portion 64 of the sheet 52 and 53 that will be formed by separating the sheets 52 and 53, and in a position such that when the rear surfaces 55 of the sheets are placed face to face as illustrated, the strip

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layers 56 of adhesive will contact the strip release coatings 70 in a generally central position; and the entire front surface 54 of each of the sheets 52 and 53 can be coated with a release coating 71 (which coating 71 is also not needed if the adhesive is low tack). Like the layers 17 of pressure-sensitive adhesive on the sheets 12 and 13, the layers 57 of pressure-sensitive adhesive on the sheets 52 and 53 are in the form of spaced strips of the adhesive that extend transversely of the sheets parallel to their opposite edges 66 and 67 with each strip being adjacent and extending along an edge of a portion 64 of the sheet that will be formed by separating the sheets 52 and 53 along the paths of weakness 63.

The sheet assembly 50 also includes indicating means for indicating the orientation of the layers 56 of pressure-sensitive adhesive between the sheets 52 and 53 the sheet assembly 50. As illustrated that means for indicating the orientation of the layers 56 of pressure-sensitive adhesive is provided in two ways, (1) by end portions of both sheets 52 and 53 adjacent their edges 66 extending past the adjacent edge 67 of the other sheet 52 or 53, and (2) by providing a mark (e.g., an arrow) or indicia (e.g., written instructions) 68 on those projecting portions of the sheets 52 and 53. Alternatively, one of the sheets 12 or 13 could be notched and indicia may be printed on the other sheet in the notch, a projecting portion of one of the sheets 52 or 53 may be used without indicia, or a mark or indicia may be used alone on the front surface 14 and at the edge of either of the sheets 12 or 13, or the sheet assembly may be made without such indicating means.

FIG. 9 illustrates a third embodiment of a sheet assembly 80 according to the present invention that could be used in the methods illustrated in FIGS. 1 and 2, which sheet assembly 80 is essentially the same as the sheet assembly 50 illustrated in FIG. 8 with similar parts being similarly numbered except for the addition of the suffix "a" except that no indicating means is provided, no layers of release coating are provided on the front surfaces of the sheets and no layer of release coating is provided adjacent one of the layers 56a of adhesive adjacent one end of the sheet assembly 80 on the sheet 53a. Thus, one of the sheets 52a of the sheet assembly 80 has a release coating on all of its nonadhesive bearing areas that will be contacted by layers 56a of adhesive and the other sheet 53a of the sheet assembly 80 has a release coating on only a portion of the nonadhesive bearing areas that will be contacted by layers 56a of adhesive so that the adhesion between at least one layer 56a of adhesive and the nonadhesive bearing area it contacts that has no release coating will adhere the sheets 52a and 53a together with sufficient firmness to facilitate printing of the front surfaces 54a of the sheets 52a and 53a without separation of the sheets 52a and 53a.

FIG. 10 illustrates an unfolded sheet assembly 90 comprising two sheets 92 and 93 separated by perforations forming a path of weakness 91 with an alternative pattern to that illustrated in FIGS. 2, 3, 8 and 9 for spaced layers 96 of pressure-sensitive adhesive in a predetermined pattern on rear surfaces 95 of the two sheets 92 and 93. That predetermined pattern is a rectangular pattern with every other rectangle in each direction being the same (i.e., either bearing a layer 96 of pressure-sensitive adhesive or being free of pressure-sensitive adhesive). The layers 96 of pressure-sensitive adhesive in the predetermined pattern on the rear surface 95 of each of the sheets 92 or 93 are adapted to contact and

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releasably adhere to the rear surface 95 of the other sheet 92 or 93 only in nonadhesive bearing areas of that rear surface 95 that are recessed with respect to the layers 96 of pressure-sensitive adhesive. Also, as illustrated, the sheet assembly 90 has release coatings 100 on the nonadhesive bearing areas of the rear surfaces 95 of the sheets 92 and 93 which are slightly larger in area than the layers 96 of adhesive, and are disposed in a position such that when the rear surfaces 95 of the sheets 92 and 93 are placed face to face while joined along the path of weakness 91, the layers 96 of adhesive will contact and will be generally centered on the release coatings 100. The entire front surface of each of the sheets 92 and 93 may optionally also be coated with a release coating. The illustrated release coatings 100 on the rear surfaces 95 and the release coatings on the front surfaces 94 of the sheets 92 and 93 may not be needed when the layers 96 of adhesive are of low-tack or repositionable adhesive, but may be useful if the layers 96 of pressure-sensitive adhesive that are more aggressive or permanent than repositionable adhesive. Pads can be made from the sheet assembly 90 using the method described above with respect to FIGS. 1 and 2 that have one or more of the layers 96 of adhesive adhering together the portions of the sheets 92 and 93 forming the pads. Even when two, four or more of the layers 96 of adhesive adhere together the portions of the sheets 92 and 93 forming the pads, corners of the sheet portions in the pads will be un-adhered to facilitate separation of those corners from the rest of the pad to initiate peeling away of a portion of one of the sheets 92 or 93 in the pad. Such separation may also be facilitated at corners of the pad adjacent the layers of adhesive by removing corners from the otherwise rectangular layers 96 of pressure-sensitive adhesive along the sides of the sheets 92 and 93.

EXAMPLE 1

An example of the sheet assembly 10 illustrated in FIGS. 3 and 4 was made and tested. Release material for the coatings 40 and 41 was prepared in accordance with the teachings in U.S. Pat. No. 5,154,962 (Mertens, et. al.), Example 41, (the content whereof is incorporated herein by reference) except the material was made in 55 gallon reactors, and the chemical composition was 47.0 percent methyl acrylate, 36.5 percent n-vinyl pyrrolidone, 5.3 percent acrylic acid, and 31.3 percent silicone macromer. The dispersion contained 12 percent tetrapolymer, 12 percent butyl carbitol, and 76 percent water. Pressure-sensitive adhesive for the coatings 16 was prepared from the teachings in European Patent Application No. 90313801.4 (Bohnel), Example 21, (the content whereof is incorporated herein by reference) with the material composition being 66.2 percent microsphere dispersion, 27.4 percent Hycar 26222, 19.3 percent deionized water, 0.7 percent ASE 95, 0.1 percent stapanol. A primer for improving the anchorage of the layers 16 of to the sheets 12 and 13 web was prepared by dissolving 4.5 parts by weight "Elvanol" (TM) 71-30 (commercially available from the DuPont Company) into 95.5 parts by weight water. To 69.0 parts by weight of the mixture, was added 35.0 parts by weight 3 micron CaCO₃. The composition was well mixed. The primer was flexographically applied to both sides of the paper sheets 12 and 13, and was dried. The release material and pressure-sensitive adhesive were flexographically printed on and dried on one face of a web of bond paper, to provide the pattern illustrated in FIGS. 3 and 4

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with the release coatings 40 in rectangles 20.6 cm wide and 3.8 cm long, and the layers 16 of pressure-sensitive adhesive in rectangles 7.1 cm wide and 3.6 cm long with adjacent aligned layers 16 being separated by 1.0 cm. The web was perforated to provide the paths of weakness illustrated in FIGS. 3 and 4. In subsequent processing, the release coating 41 was coated on the front surfaces 14 of the sheets 12 and 13 using rotogravure processing and was dried. The web was then folded and separated to form sheet assemblies 10 that were 21.6 cm wide by 27.9 cm long, and were perforated in the width every 7.0 cm. Sheet assemblies 10 were then printed in a Hewlett Packard "LaserJet III" on both sides by feeding the assembly through the machine twice. Both graphics and printed indicia were printed on the sheet assemblies 10. Subsequently, the sheets 12 and 13 of the printed sheet assemblies were peeled apart, and torn apart along the perforations or path of weakness 31 at their ends 30. The separated sheets 12 and 13 were then manually stacked and separated along the perforations or paths of weakness 33 to provide note pads of the type 42 illustrated in FIG. 5. Similar printed and separated sheets 12 and 13 were manually stacked and separated along the perforations or paths of weakness 33 to provide note pads of the type 44 illustrated in FIG. 6.

EXAMPLE 2

Examples of the sheet assemblies 10 were made using the same bond paper, adhesive, primer, and coating methods and other method described in Example 1, except that the release material used in the coatings 40 on the rear surface 15 was the heat curable silicone, 96 percent "Syl-Off" (TM) 7676 and 4 percent "Syl-Off" (TM) 7628 (commercially available from Dow Corning Corp.), and no release coating was applied to the front surface 14 of the sheets 12 and 13. These sheet assemblies were printed and converted into pads in the same manner described in Example 1 and were found to perform well.

EXAMPLE 3

Example sheet assemblies generally of the type 10 illustrated in FIGS. 3 and 4 were made using sheets 12 and 13 of carbonless paper of the type commercially available from 3M under the trademark "Scotchmark". A release material for the coating 40 was prepared by dissolving 12 g "Syl-Off" TM 7610 and 0.5 g "Syl-Off" TM 7611 (both commercially available from Dow Corning Corp.) into 88 g toluene. An adhesive material for the layers 16 of adhesive was prepared from a suspension in organic solvent of 10 parts of the copolymer of 95% isooctyl acrylate and 5% acrylic acid and 90 parts of tacky elastomeric copolymer microspheres ranging in diameter from about 10 to 150 micrometers. The adhesive was coated from about 13 percent solids content using a slot with an 0.10 mm orifice to a silicone treated web and dried to form a transfer tape. A swab was prepared to manually apply the release coating in various configurations. The swab used a 3 cm wide paper towel attached to a tongue depressor. Laser pre-perforated carbonless paper was preprinted and cut to form sheets 21.6 cm wide and 29.2 cm long, each with a perforation 13 mm from the top of the sheet. Two sets of carbonless forms with a top sheet and a second copy sheet were coated with silicone along the terminal edge opposite the perforation. The silicone composition was cured in heat. To both top sheets was applied a 10 mm long strip of transfer tape 20.3 cm wide, along the terminal

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edge next to the perforation. The silicone web was removed to expose the adhesive. The sheets 12 and 13 were aligned and laminated such that the layer of adhesive 16 on one sheet contacted the release coating of the adjacent sheet. To the bottom sheets was applied a 10 mm long strip of transfer tape 14 cm wide, along the terminal edge next to the perforation. The silicone web was removed to expose the adhesive. The sheets 12 and 13 were aligned and laminated such that the layer of adhesive 16 on one sheet contacted the release coating of the adjacent sheet. The assemblies were found to be stable when handled. Both assemblies were printed in a Hewlett Packard "LaserJet III" laser printer. The assemblies were separated and stacked into two form sets, each with top and bottom sheets. The sets were found to dispense in the manner described by U.S. Pat. No. 5,050,909.

EXAMPLE 4

An example of the sheet assembly illustrated in FIG. 9 was prepared. Two sheets 52a and 53a of bond paper were prepared with dimensions 21.6 cm wide and 14.0 cm long. A transverse perforation 63a was made at 7.0 cm of length for each sheet 52a and 53a. A 20 mm wide swab was prepared as in Example 3. A transfer tape was prepared using the adhesive composition described in Example 3, only it was coated using a 0.05 mm orifice. The adhesive was dried. The silicone from Example 3 was applied to form the coatings 70a in strips across the width of the paper sheets 52a and 53a. Two strips 70a were applied to the first sheet 52a, one along a terminal edge, and the second along the perforation 63a on its side opposite that terminal edge. One strip 70a was applied to the second sheet along the perforation 63a. Two strips of 12 mm long transfer tape were applied across the width of each sheet 52a and 53a to form the layers 56a of adhesive disposed as illustrated in FIG. 9. After the tape was laminated to the sheets 52a and 53a, the release liner was removed to uncover the adhesive. The rear surfaces 55a of the sheets 52a and 53a were adhered together resulting in three layers 56a of adhesive contacting release coatings 70a of silicone and one layer 56a of adhesive strip contacting the uncoated inner surface 55a of the sheet 53a as is illustrated in FIG. 9. The sheet assembly 80 was found to be stable, and was printed in a Hewlett Packard "LaserJet III" laser printer.

EXAMPLE 5

Ten example sheet assemblies 10 were prepared as described above in Example 1. Artwork on a pattern sheet was prepared using computer software and a laser printer. The artwork consisted of eight (8) images positioned on the pattern sheet so that it would generally align with the portions 34 of the sheets 12 and 13 defined by the perforations or paths of weakness 33. Two copies of the pattern sheet were printed by the laser printer and used for printing both front surfaces 14 of the sheet assemblies 10 on a Lanier 6272 copier used in duplex mode. The printed sheets 12 and 13 of the sheet assemblies 10 were sequentially peeled apart and separated at the path of weakness 31. The sheets 12 and 13 were stacked into a master stack 26 as illustrated in FIG. 2 using a box lid elevated at one corner as the stacking frame 25 so that sheets were aligned on the stack 26 against the corner of the box lid opposite its elevated corner. The master stack 26 was cut into 16

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individual note stacks 10.8 cm wide and 7.0 cm tall using a guillotine cutter 28.

EXAMPLE 6

Examples of the sheet assembly 90 illustrated in FIG. 10 were made using the materials and processes described in Example 1. The sheet assemblies 90 made were 21.6 cm wide and 27.9 cm long. The layers 96 of adhesive were each about 4.1 cm wide and 2.5 cm long. The sheet assemblies 90 were printed using the artwork illustrated in FIG. 7 using a Lanier 6272 copier in duplex mode. The sheets 92 and 93 of the printed sheet assemblies 90 were separated and stacked as illustrated in FIG. 2 with the layers 96 of adhesive on the sheets 92 and 93 adjacent the front surfaces 94 of the adjacent sheet by aligning corners of the separated sheets 92 and 93 in the corner of a tray, which tray was elevated on its side diagonally opposite the corner against which the sheets were aligned to provide a gravitational aid in alignment. The master stack of the sheets 92 and 93 thus formed was then cut along cut lines 110 illustrated in FIG. 7 to form pads of different sizes. The portions of the sheets 92 and 93 in each pad had at least one layer 96 of adhesive to adhere those portions together, and the sheet portions in the larger pads which had two or more diagonally disposed layers 96 of adhesive which adhered them together.

The present invention has now been described with reference to several embodiments thereof. It will be apparent to those skilled in the art that many changes can be made in the embodiments described without departing from the scope of the present invention. Thus the scope of the present invention should not be limited to the methods and structures described in this application, but only by the methods and structures described by the language of the claims and the equivalents of those methods and structures.

We claim:

1. A method for making custom printed notes, said method comprising the steps of:
 - providing a sheet assembly comprising first and second sheets each having major front and rear surfaces, and layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of the sheets, the layers of pressure-sensitive adhesive on the rear surface of each of the sheets contacting and being releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas that are recessed with respect to the layers of pressure-sensitive adhesive;
 - printing indicia on at least one of the front surfaces of the sheets in the sheet assembly;
 - separating the sheets along predetermined planes normal to and extending across the major surfaces of the sheets to form the custom printed notes.
2. A method for making custom printed note pads, said method comprising the steps of:
 - providing a plurality of sheet assemblies each comprising first and second sheets each having major front and rear surfaces and opposite edges, and layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of said sheets, said layers of pressure-sensitive adhesive on the rear surface of each of said sheets in each of said sheet assemblies contacting and being releasably adhered to the rear surface of the other sheet only in nonadhesive bearing areas that are recessed with respect to the layers of pressure-sensitive

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adhesive, and being releasably adherable to the front surfaces of the sheets;

printing indicia on at least one of the front surfaces of the sheets in at least some of the sheet assemblies;

separating the sheets in the sheet assemblies after said printing step; and

stacking the separated sheets to adhere the layers of pressure-sensitive adhesive on the rear surfaces of the sheets to the front surfaces of the sheets with the layers of adhesive in a predetermined orientation with respect to each other.

3. A method for making custom printed note pads according to claim 2 wherein said method further includes the step of separating the stacked sheets along predetermined planes normal to and extending across the major surfaces of the stacked sheets to form the custom printed note pads.

4. A method for making custom printed note pads according to claim 2 wherein said providing step provides the layers of pressure-sensitive adhesive on the rear surfaces of each of said sheets in strips aligned with predetermined ones of the planes along which the stacked sheets are separated in the separating step such that each of the sheet portions in each of the custom printed note pads has a portion of one of the strips of adhesive along a corresponding edge of the pad.

5. A method for making custom printed note pads according to claim 2 wherein said providing step provides the layers of pressure-sensitive adhesive on the rear surfaces of said sheets in strips aligned with the predetermined ones of the planes along which the stacked sheets are separated in the separating step such that each successive sheet portion in each of the custom printed note pads has a portion of one of the strips of adhesive along an opposite edge of the pad.

6. A sheet assembly adapted to be printed on one or both sides and subsequently converted into a plurality of sheets each having printing on one surface and a small area of pressure-sensitive adhesive on an opposite surface, said sheet assembly comprising

first and second sheets each having major front and rear surfaces and opposite edges, and

layers of pressure-sensitive adhesive in a predetermined pattern on the rear surface of each of said sheets,

said pattern of pressure-sensitive adhesive on the rear major surface of each of said sheets contacting and being releasably adhered to the rear major surface of the other sheet only in nonadhesive areas that are recessed with respect to the pattern of pressure-sensitive adhesive.

7. A sheet assembly according to claim 6 wherein said adhesive is a low-tack pressure-sensitive adhesive and said nonadhesive bearing areas are free of release coating.

8. A sheet assembly according to claim 7 wherein said low-tack pressure-sensitive adhesive comprises tacky, elastomeric copolymer microspheres.

9. A sheet assembly according to claim 6 further including a release coating on said nonadhesive bearing areas.

10. A sheet assembly according to claim 6 further including a release material on the front surface of one or both of said sheets.

11. A sheet assembly according to claim 10 wherein said release material comprises an indicia-receptive polymer.

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12. A sheet assembly according to claim 6 wherein said sheet assembly further includes means along one of said edges for indicating the orientation of the layers of pressure-sensitive adhesive in the sheet assembly.

13. A sheet assembly according to claim 12 wherein a portion of said first sheet adjacent one edge of said first sheet extends past the adjacent edge of said second sheet to provide said means along one of said edges for indicating the orientation of the layers of pressure-sensitive adhesive in the sheet assembly.

14. A sheet assembly according to claim 6 wherein said sheets are attached along adjacent edges and have a path of weakness along said joined edges so that the sheets are sufficiently joined together along said edges to facilitate printing of the front surfaces of the sheets without separation of the sheets.

15. A sheet assembly according to claim 6 having a release coating on all of the nonadhesive bearing areas of one of said sheets and having a release coating on

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only a portion of the nonadhesive bearing areas of the other of said sheets so that the adhesion between at least one layer of adhesive and one nonadhesive bearing area that has no release coating will adhere the sheets together with sufficient firmness to facilitate printing of the front surfaces of the sheets without separation of the sheets.

16. A sheet assembly according to claim 6 wherein said sheets are of material selected from the group consisting of plane paper, bond paper, clay-coated paper, opaque polymeric material, translucent polymeric material and carbonless paper.

17. A sheet assembly according to claim 6 wherein the total area covered by the layers of pressure-sensitive adhesive on both of said sheets is less than 50 percent of the total surface areas of the rear surfaces of both of said sheets.

* * * * *

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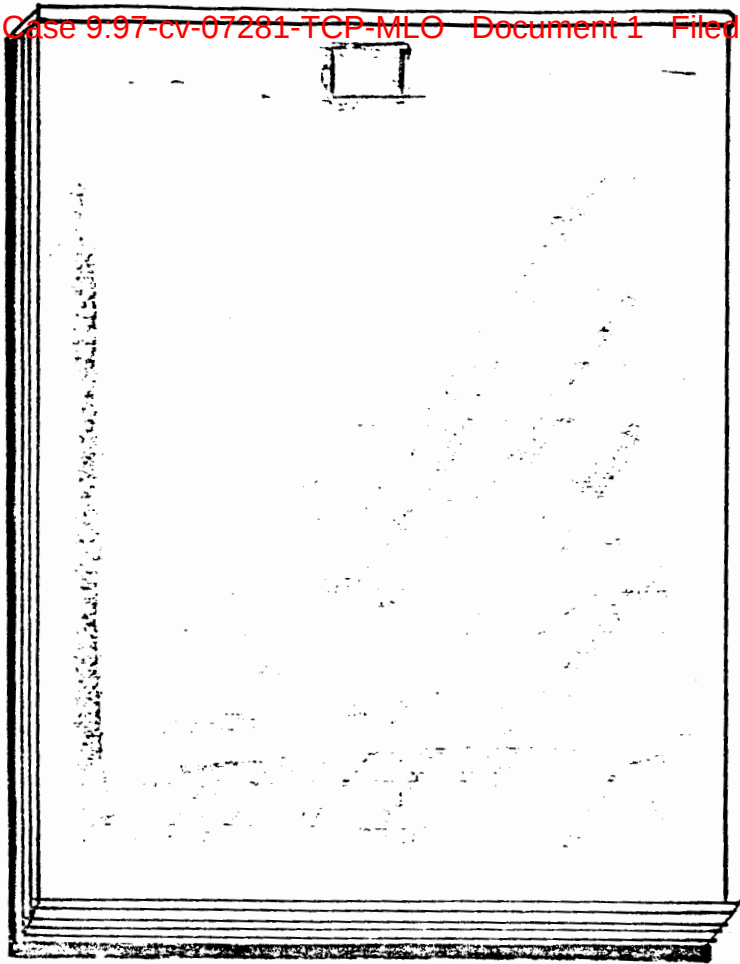
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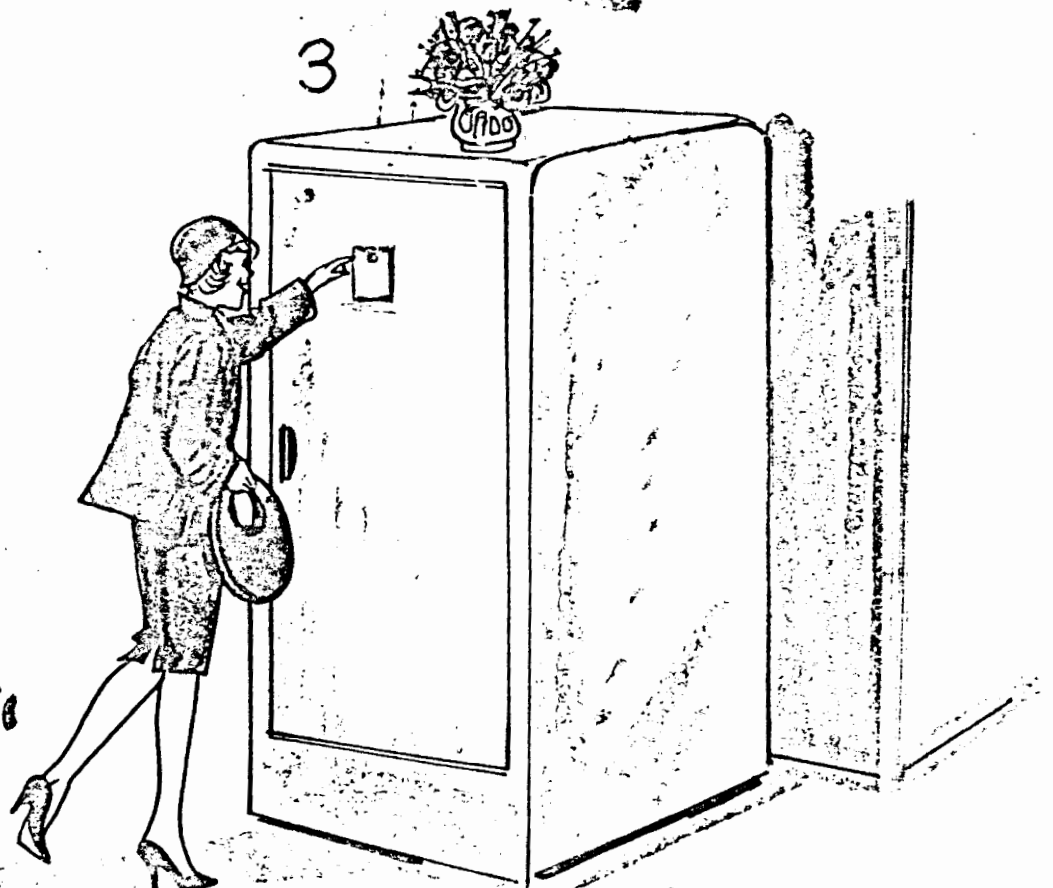
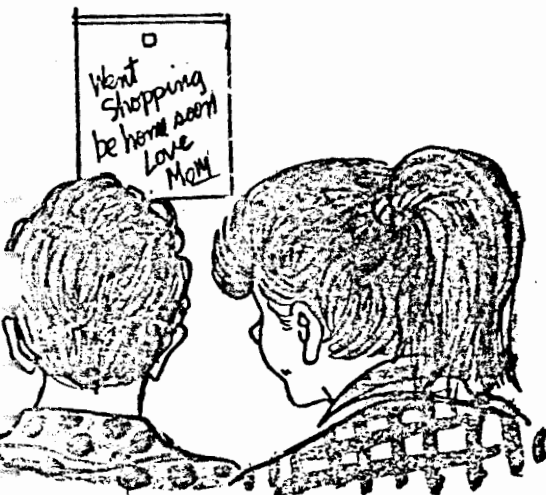
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3



5

insti-sta



THE MAGIC TOUCH

YOUR INVITATION
TO INSTANT PROFIT!
IT'S PRACTICAL, IT'S ATTRACTIVE,
IT'S EASY TO HANDLE...

JUST JOT DOWN YOUR MEMO, TEAR OFF, PLACE ANYWHERE,
TOUCH THE MAGIC "M" AND PRESTO IT STAYS. IT'S THAT EASY.
THIS NOW ALLOWS YOU TO HANG YOUR MEMO WITHOUT THE
USE OF TAPES, PINS OR MAGNETS.

WITH OUR EXCITING ADVERTISING
CAMPAIGN REACHING A MARKET
THAT'S ENDLESS...IT ADDS UP TO BIG
PROFITS! THAT'S NOT MAGIC...
THAT'S GOOD BUSINESS.

FOR COMPLETE INFORMATION WRITE TO:

PRESS-ON MEMO LTD. P.O. BOX 302 ROCKVILLE CENTRE, NEW YORK 11570



M THE MAGIC TOUCH

JUST JOT DOWN YOUR MEMO, TEAR OFF,



PLACE ANYWHERE, TOUCH THE MAGIC "M"
AND PRESTO IT STAYS. IT'S THAT EASY.

THE FANTASTIC NEW
TACKY SPRAY

**STICK-
EM-UP**

INSTANT
PRESSURE
SENSITIVE
EFFECT



JUST
SPRAY IT
AND STICK-
EM-UP!

Almost any surface
Non-Staining
Simple to use

NET WT. 16 OZ.

THE FANTASTIC NEW
TACKY SPRAY

**STICK-
EM-UP**

INSTANT
PRESSURE
SENSITIVE
EFFECT

JUST
SPRAY IT
AND STICK-
EM-UP!



Non-
Flammable

CAUTION:
Keep out of
reach of
children

NET WT. 7 OZ.

**STICK-
EM-UP**

THE FANTASTIC TACKY SPRAY

Non-Flammable
Almost any surface
Non-staining • Simple to use

USES:

REPAIR • MOUNT
SPICE • ATTACH
SEAL • FASTEN
DECORATE

USERS:

ARTS & CRAFTS
DECOUPAGE • ARTISTS
PHOTOGRAPHERS
PICTURE FRAMERS
DO-IT-YOURSELFERS

ART & DISPLAY WORK:

Mount Signs, Lettering,
Fabrics, Cork,
Cardboard, Foil, Wood,
Plastic Sheeting, etc.

HOBBY & CRAFT:

Adhere Glitter and Sand,
Decoupage and Collage

OTHER USES:

Adhere Leather, Fabric,
Wallpaper, Shelfpaper,
Labels, Felt Padding,
Carpet Squares,
Mount Posters,
Pictures, Memos, etc.

DIRECTIONS

Shake well before using. Expose under part of surface you wish to make pressure sensitive. Holding can 12" away, spray surface. Do not overspray and allow a few seconds to dry. Your surface is now pressure sensitive. Press lightly on top of surface and it will stick. Item can be lifted and repositioned with ease.

AFTER USING—Turn can upside down and press tip until spray is clear of adhesive.

PERMANENT BOND—When using as a permanent bond, spray area and apply before allowing to dry.

NON-PERMANENT—Spray area, allow to dry before applying.

CAUTION:

Use with adequate ventilation. Avoid prolonged inhalation of vapor. Contents of can under pressure. Do not dispose of can in incinerator. Store below 120° F.

NOTICE TO PURCHASER: Manufacturer's only obligation shall be to replace such quantity of the product proved to be defective. User shall determine the suitability of the product for his intended use and assume all risk and liability in connection therewith.

**STICK-
EM-UP**

BARRY ALAN PRODUCTS INC.
31 South Grove Street
Freeport, L.I., N.Y. 11520
Made in U.S.A.

THE FANTASTIC NEW
TACKY SPRAY

**STICK-
EM-UP**

INSTANT
PRESSURE
SENSITIVE
EFFECT

JUST
SPRAY IT
AND STICK-
EM-UP!



Non-
Flammable

CAUTION:
Keep out of
reach of
children

NET WT. 7 OZ.

**STICK-
EM-UP**

THE FANTASTIC TACKY SPRAY

DIRECTIONS

Expose under part of surface you wish to make pressure sensitive. Holding can 12" away, spray surface. Do not overspray and allow a few seconds to dry. Your surface is now pressure sensitive. Press lightly on top of surface and it will stick. Item can be lifted and repositioned with ease.

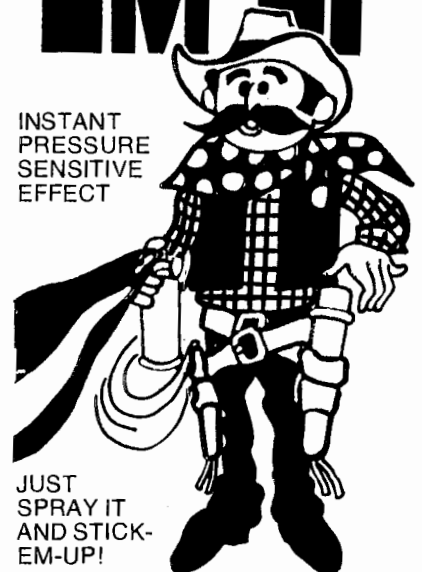
CAUTION:

Use with adequate ventilation. Avoid prolonged inhalation of vapor. Contents of can under pressure. Do not dispose of can in incinerator. Store below 120° F.

THE FANTASTIC NEW
TACKY SPRAY

**STICK-
EM-UP**

INSTANT
PRESSURE
SENSITIVE
EFFECT



JUST
SPRAY IT
AND STICK-
EM-UP!

Almost any surface
Non-Staining
Simple to use

NATIONAL MAIL ORDER MERCHANDISE SHOW

February 11, 1975

Mr. Allen Amron
Press-on Memo, Ltd.
26 Middleneck Rd.
Great Neck, L.I., New York 11021

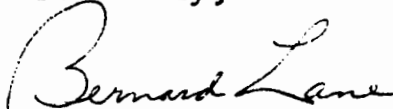
Dear Mr. Amron:

Thank you for your telephone inquiry yesterday. Enclosed is the information on the show. It includes a floor plan marked up to show booth #85 which has been changed to an 8 ft. by 8 ft. type "A" booth. There is a small booth on the right hand side which will probably be occupied by a company having one product. As you can see, booth #85 is very well located and will receive maximum traffic.

I am also circling booths #30 and #35 which are available in the Red Room. Please note that the Red Room is adjacent to the main stairway from the lobby.

Look forward to hearing from you in the very near future, so that we can put the 1975 National Mail Order Merchandise Show to work for Press-on Memo, Ltd.

Sincerely,



Bernard Lane
President

BL/ar
enclosures

THE MAGIC • TOUCH



PRESS-ON MEMO LTD.

P.O. BOX 302

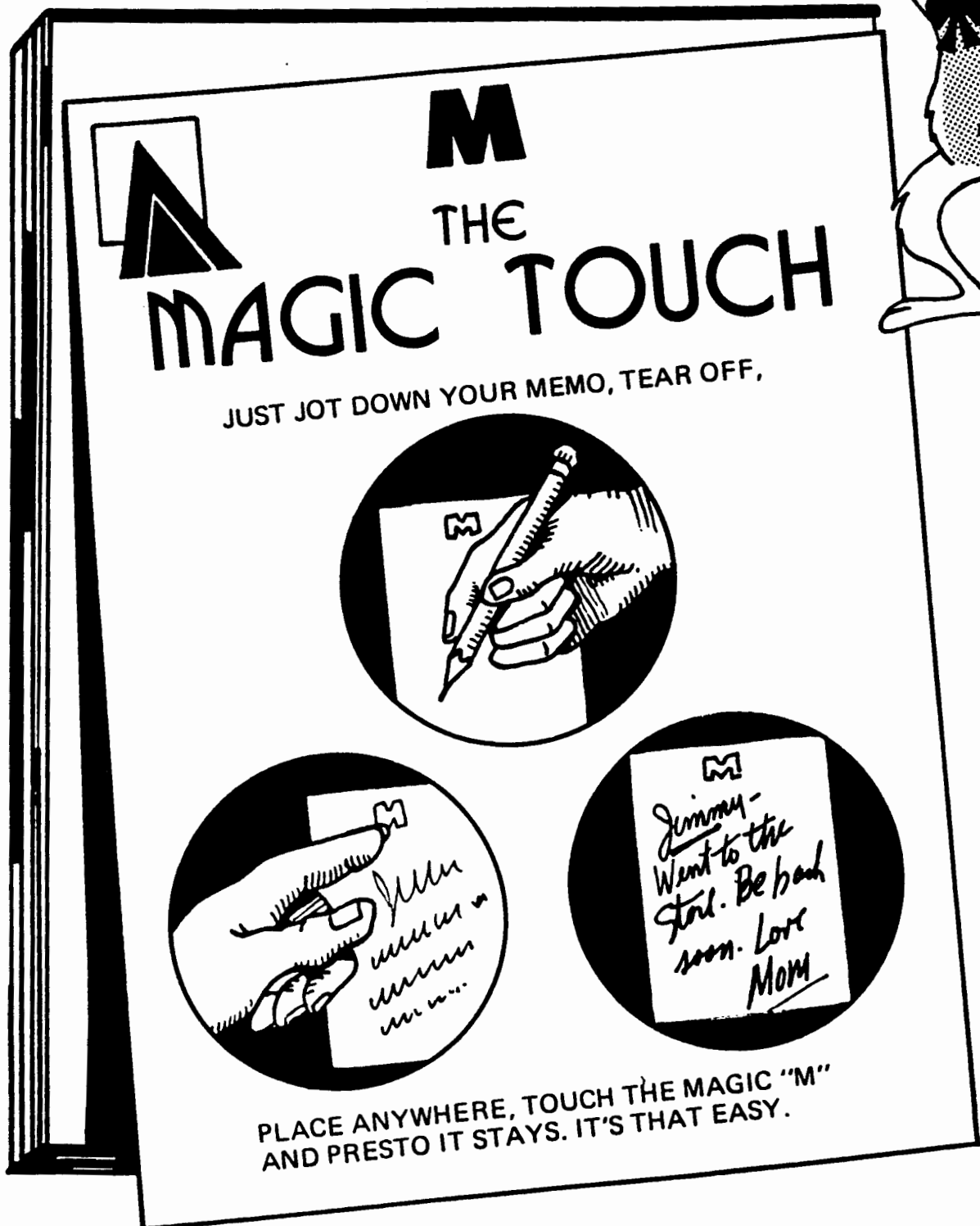
ROCKVILLE CENTRE, NEW YORK 11570

**Actual sample of the envelope
used in 1974 mass mailing**

ATTENTION ATT: STATIONERY BUYER

**A REVOLUTIONARY INVENTION IN STATIONARY
THAT BRINGS BIG PROFITS!**

Presto!



ACTUAL SIZE

A silent secretary right at your fingertips, for the home or at business, that allows you to hang your memo without the use of tapes, pins or magnets. It's practical, it's attractive, it's easy to handle and costs very little. It also makes a nice gift.

FOR COMPLETE INFORMATION WRITE TO:

PRESS-ON MEMO :



THE MAGIC • TOUCH

YOUR INVITATION
TO INSTANT PROFIT!
IT'S PRACTICAL, IT'S ATTRACTIVE.
IT'S EASY TO HANDLE...

JUST JOT DOWN YOUR MEMO, TEAR OFF, PLACE ANYWHERE,
TOUCH THE MAGIC "M" AND PRESTO IT STAYS. IT'S THAT EASY.
THIS NOW ALLOWS YOU TO HANG YOUR MEMO WITHOUT THE
USE OF TAPES, PINS OR MAGNETS.

WITH OUR EXCITING ADVERTISING
CAMPAIGN REACHING A MARKET
THAT'S ENDLESS...IT ADDS UP TO BIG
PROFITS! THAT'S NOT MAGIC...
THAT'S GOOD BUSINESS.

FOR COMPLETE INFORMATION WRITE TO:
PRESS-ON MEMO LTD. P.O. BOX 302 ROCKVILLE CENTRE, NEW YORK 11570

**Actual sample of a self stick
repositionable, reusable Memo sheet
sent out in 1974 mass mailing**

Int. Cl.: 16

Prior U.S. Cl.: 37

United States Patent Office

Reg. No. 1,046,353
Registered Aug. 17, 1976

TRADEMARK
Principal Register

POST-IT

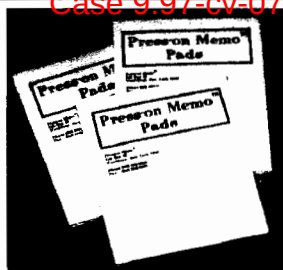
Minnesota Mining and Manufacturing Company (Delaware corporation)
3M Center
St. Paul, Minn. 55101

For: PAPER AND CARDBOARD SHEET MATERIAL HAVING ADHESIVE COATING ON BOTH SIDES THEREOF FOR ATTACHMENT TO WALLS OR OTHER VERTICAL SURFACES TO HOLD DISPLAYS OR OTHER MESSAGES IN PLACE, in CLASS 16 (U.S. CL. 37).

First use Sept. 25, 1974; in commerce Sept. 25, 1974.

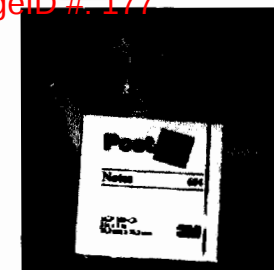
Ser. No. 72,879, filed Dec. 29, 1975.

P. P. GRALNICK, Supervisory Examiner
G. H. FECHTER, Examiner

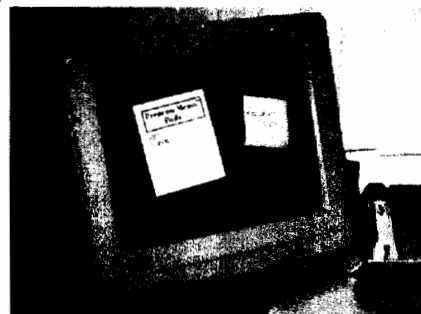


Press-on Memo™

Product Characteristics Comparision Chart...



Post-it Note®



1. Memo Pad
2. Self stick
3. Repositionable
4. Removable
5. Reusable
6. Press to hang
7. Padded by itself
8. Used as Markers
9. Adhesive will not transfer.
10. Memo Sheet
11. Adhesive applied by spray process to form islands
12. Amron put into use in 1974.



1. Note Pad
2. Self stick
3. Repositionable
4. Removable
5. Reusable
6. Press to hang
7. Padded by itself
8. Used as Markers
9. Adhesive will not transfer.
10. Note Sheet
11. Adhesive applied by spray process to form islands
12. 3M put into use in 1981.

The only difference is that Amron did it 7 years earlier than 3M....

STATE OF NEW YORK :
: ss.:
COUNTY OF NASSAU :

AFFIDAVIT

Alan B. Amron, being duly sworn, deposes and says:

I am Alan Amron Pro Se Plaintiff in the attached complaint and although it took me some time to gather evidence I would need to start this action, I now can say that in December 1973 I conceived, created, invented and in July of 1974 I put into public use for license and or sale a revolutionary new stationery item called Press-on Memo pads, a self sticking repositionable, removable and reusable memo pad with its newly developed adhesive. I then contacted, and visited with, my patent attorney Mr. Charles Marks located at 286 Fifth Avenue in New York City. He instructed me to have an artist do a rendering of my conception and I should write a description of my new invention for the filing of a Patent and a Trademark.

1. I needed capital to fund this project so I took in a financial partner by the name of Jeffrey Brown. (see Exhibit #12 of the complaint)

2. In November 1973 I contracted a chemical engineering and Development Company located at 875 North Michigan Avenue in Chicago Illinois, Dr. David Young Hon. AIC, to develop a less tacky adhesive, as per my specifications, for my Press-on Memo pads. He sent me a number of samples to test, and

finally I found one that gave me the result I was looking for. Our objective was for it to be strong enough to hold together a stack of 50 sheets in a pad, and yet weak enough not to ever dry up and glue those sheets together permanently. Then we tested each sheet to stick and re-stick a number of times on telephones, walls, papers etc. We called this new adhesive Tactless, Contact-less and finally stayed with "Stickem Up" a repositionable, reusable, low tack removable pressure sensitive spray adhesive for my Press-on Memo sheet pads. (see Exhibit #1 & #1a of the complaint)

3. In February of 1974 I contracted Steven Grossman, a graphic artist who did work for the Benihana restaurants, to do an artist rendering of my invention. (see Exhibit #19 of the complaint)

4. In March of 1974 I had Steven Grossman do mechanicals for printing flyers, envelopes and actual Press-on Memo sheets to make the pads. (see Exhibit #3a, #3b and #3c of the complaint)

5. In April of 1974 I contracted Dave Warren of Kroma Lithographers in New York City to print Press-on Memo sheets, flyers and envelopes for mailings and handing out. (see Exhibit #3a, #3b and #3c of the complaint)

6. I actually stood in my garage spraying each of those 2,000 Press-on Memo sheets, and then brought them back to Dave Warren's office so he could deliver them, with the

envelopes and flyers, to the Mass Mailer. (see Exhibits #1b & #1c of the complaint adhesive comparison charts)

7. In June of 1974 I contacted a company in New York City called Mass Mailings, Mr. Sol Rebach, to do a mass mailing to the entire stationery industry, which included 3M. Mr. Sol Rebach told me there were approximately 1900 to 2000 possible stationery top level executives on his stationery industry mailing list, which included manufacturers, retail store chains, wholesale distributors. He needed 2000 envelopes, flyers and samples of Press-on Memos from us to be delivered to him at least one week before he can do the mailing. They were delivered to him directly from Dave Warren's office, the printer, and then mailed out by mass mailing.

8. On July 22, 1974 I personally opened a Post Office box under the Corporate name of Press-on Memo Lt. in anticipation of the responses from the mass mailing. (see Exhibit #14 of the complaint)

9. I was contacted in July 1974 by my general counsel, Mr. Michael Solomon, Esq. confirming that we had secured the New York State Corporate name of "Press-on Memo Ltd." for this new invention. (see Exhibit #13 of the complaint)

10. We received a number of responses requesting prices and delivery. We told everyone that called or wrote in that it would be a \$1.19 retail for three 50 sheet pads of Press

on Memos. Delivery was immediately for smaller quantities, and three to four weeks for larger quantities.

11. I, Alan Amron the Plaintiff in this matter, personally exhibited in the International Inventor Expo at the Americana hotel in New York City, and gave a demonstration of my "Press-on Memo" pads and its' "Stickem up adhesive" spray we used on the those pads (self sticking, repositionable, reusable, removable memo sheets and adhesive) to a representative who claimed to be from the 3M company, amongst others, and I gave samples and flyers for them to consider either (i) buying the idea out right, (ii) buying from me as a supplier or (iii) paying me a royalty on an on going basis. (see Exhibit #27 a-d in the complaint)

12. In March of 1975 I started to sell the Stickem up tacky spray in cans, everyone that I showed this newly developed reusable, repositionable and removable self sticking adhesive spray to went crazy for it, and not only for use on the Press-on Memo sheets but on photos etc. (see Exhibit # 27 a-b-c-d, #28 and #28a, #29 a-s as proof of sales to the public for this new adhesive)

13. I did in fact make public use and offered for sale my invention conception for a self stick, removable, reusable repositionable Press-on memo pad, and its' newly developed adhesive, in 1974 to the following people and organizations;

Dan Simon of Pickwick Stationery, Jeffrey Brown,
Michael Solomon, Esq., Charles Marks Esq.,

Dr. David Young Hon. AIC., New York State Division of Corporations, The United States Post Office, J. Carlton, The Elmers Glue Company Wholesale Adhesives Division, The Invention EXPO attendees (about 30 I personally spoke with including the 3M representative) at the Sheridan Hotel in New York Jay Norris, Herman Amron, Gloria Amron, Ivan Amron, Eileen Amron, Fredi Amron, Steven Grossman, Dave Warren, Dave Warren's son, Dave Warren's wife, Sol Rebach, Dick Freudenhiem, Bernard Lane, Marsha Bliss, Dr. Richard Kaufman, Dave DiVerde, Muriel Simon, Fred Lane, Steven Bliss, Ronald Lane, Donald Miller, Sheldon Friedland, Milton Weinstock, Eleanor Friedland, Gary Liebling, Jay Cohen from the Modern Dykman Camera store, etc.

(see Exhibits #28, #28a and #29 a-s for additional companies who had purchased the specially developed adhesive that was made for the Press-on Memo pads)

WHEREAS, I am the original creator and inventor of the very first memo/note pad and its' repositionable low tack adhesive that is self sticking, repositionable, reusable, removable, and having shown here that my conception date of December 1973, for this invention, is at least one year prior to any Patents applied for by the Defendant 3M, by assignment. Therefore all Patents issued to 3M, relating to the products called Post-it Notes and their related adhesives that are low tack self sticking, repositionable, reusable and removable, by assignment, should now be declared invalid based on their violation of PTO Rule 56 and Amron's earlier conception and put into use date.

Sworn to before me this
21 st day of November 1997

Alan Amron

Notary Public



US005571617A

United States Patent [19]**Cooprider et al.**[11] **Patent Number:** **5,571,617**[45] **Date of Patent:** **Nov. 5, 1996**

[54] **PRESSURE SENSITIVE ADHESIVE
COMPRISING TACKY SURFACE ACTIVE
MICROSPHERES**

[75] **Inventors:** **Terrence E. Cooprider**, Woodbury;
Dale O. Bailey, White Bear Lake, both
of Minn.; **Ronald W. Most**, River Falls,
Wis.

[73] **Assignee:** **Minnesota Mining and
Manufacturing Company**, St. Paul,
Minn.

[21] **Appl. No.:** **270,179**

[22] **Filed:** **Jul. 1, 1994**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 174,620, Dec. 28, 1993,
abandoned, which is a continuation of Ser. No. 52,386, Apr.
23, 1993, abandoned.

[51] **Int. Cl.^o** **B32B 7/12; B32B 27/30**

[52] **U.S. Cl.** **428/341; 428/40.2; 428/41.5;**
428/327; 428/343; 428/354; 428/355

[58] **Field of Search** **428/41, 42, 355,**
428/354, 343, 327, 40, 341

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Primary Examiner—Peter A. Szekely

Attorney, Agent, or Firm—Gary L. Griswold; Walter N.
Kim; Carolyn V. Peters

[57] **ABSTRACT**

A coated sheet material comprising a backing and a coating of repositionable pressure-sensitive adhesive comprising a plurality of solid microspheres, a polymeric stabilizer and an surfactant. Processes for preparing solid microspheres are also disclosed.

11 Claims, No Drawings

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PRESSURE SENSITIVE ADHESIVE COMPRISING TACKY SURFACE ACTIVE MICROSPHERES

This application is a continuation-in-part of application Ser. No. 08/174,620, filed Dec. 28, 1993, now abandoned which is a continuation of application Ser. No. 08/052,386, filed Apr. 23, 1993, now abandoned.

TECHNICAL FIELD

This invention relates to repositionable adhesives, repositionable adhesive-coated sheet materials and processes for preparing repositionable adhesives.

BACKGROUND OF THE INVENTION

Positionable adhesives are those that allow for the placement of an article containing such an adhesive onto a receptor in an exact position, because the article can be adjusted relative to the receptor after initial placement.

In some instances, the adhesive can be designated repositionable or repeatedly reusable. As used herein, the term "repositionable" refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability. Such adhesives exhibit aggressive tack but low peel adhesion properties, thus allowing repeated reusability. Commercial products such as the 3M brand Post-ItTM Notes display such adhesive characteristics.

Solid, inherently tacky, elastomeric microspheres are known in the art to be useful in repositionable adhesive applications. Microsphere-based adhesives are thought to perform well in such applications at least in part due to their "self-cleaning" nature wherein substrate contaminants tend to be pushed aside and trapped between the microspheres as the adhesive is applied. Upon removal, the adhesive still presents a relatively uncontaminated surface for reapplication to the substrate.

One problem associated with these types of adhesives has been microsphere transfer, i.e., microsphere loss to a receptor. That is, microsphere loss from a substrate on which the microsphere has been positioned to a surface to which the substrate has been adhered by the microsphere. To alleviate this problem, binders or primers have been utilized.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a sheet material comprising a backing and a coating of repositionable pressure-sensitive adhesive coated on at least one major surface of the backing, the adhesive comprising

i) a plurality of polymeric, solid, elastomeric microspheres that are the reaction product of reactants comprising polymerizable starting materials comprising at least one C_4-C_{14} alkyl (meth)acrylate monomer and at least one polar comonomer which, if the polar comonomer comprises a dissociable proton, has no dissociable proton having a K_a of greater than 10^{-3} ;

ii) a polymeric stabilizer in an amount of between about 0.1 and about 3 parts by weight per 100 parts by weight of the microspheres (preferably about 0.5 to about 2 parts by weight per 100 parts by weight of the microspheres); and

iii) a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of the microspheres (preferably about no greater than 3 parts by weight and most preferably in the range of 0.1 to about 1.5 parts by weight per 100 parts by weight of the microspheres). As used in this

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application, the notation "(meth)acrylate" refers to acrylate and methacrylate.

In another aspect, the present invention provides a one step suspension polymerization process for preparing polymeric, solid, elastomeric microspheres comprising the steps of:

a) stirring or agitating a mixture comprising polymerizable monomer starting materials comprising at least one C_4-C_{14} alkyl (meth)acrylate monomer and a polar comonomer which, if the polar comonomer comprises a dissociable proton, has no dissociable proton having a K_a greater than 10^{-3} ; an initiator for the polymerizable monomer starting materials; a polymeric stabilizer in an amount in the range of 0.1 to about 3 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of polymerizable monomer, preferably no greater than about 3 parts by weight and most preferably in the range of 0.1 to 1.5 parts by weight; and water to form an oil in water suspension; and

b) polymerizing the (meth)acrylate monomer(s) and the polar comonomer(s); wherein solid microspheres are provided.

In yet another aspect, the present invention provides a two-step suspension polymerization process for preparing polymeric, solid, elastomeric microspheres from polymerizable monomer starting materials, the process comprising the steps of:

a) stirring or agitating a mixture comprising at least one C_4-C_{14} alkyl (meth)acrylate monomer; an initiator for the monomer; a polymeric stabilizer in an amount of about 0.1 to about 3 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of the polymerizable monomer starting materials, preferably no greater than 3 parts by weight and most preferably in the range of 0.5 to 2 parts by weight; and water to form an oil in water suspension;

b) at least partially polymerizing the polymerizable monomer starting materials;

c) adding to the suspension a polar comonomer(s) which, if the polar comonomer(s) comprise a dissociable proton, have no dissociable proton having a K_a greater than 10^{-3} ; and

d) continuing the polymerization of the polymerizable monomer starting materials; wherein microspheres are provided.

It is desirable to make a pressure sensitive adhesive with improved adhesion and yet repositionable without fiber pick-up. There are several criteria indicated for such an adhesive.

First, a solid, well-formed microsphere is desirable because such microspheres provide repositionability at high microsphere coating weights because of improved topology of the coating surface.

Second, it is desirable to have improved adhesion to particular surfaces, such that the adhesive strength remains constant or slightly builds after a period of time.

Third, it is desirable that the impurities in the coating solution, such as surfactants, polymeric protective colloids, be minimized to maintain the high adhesion level. Typically, this would result in coatings that are process unstable because of shear. Surprisingly, this problem is eliminated and the microspheres of the present invention improve process stability because of shear in fluid handling.

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Fourth, it is desirable to develop a microsphere adhesive that adheres to a substrate or backing and easily removes from applied surfaces without transferring or leaving an adhesive residue on the applied surface.

The microsphere-containing adhesives prepared according to the processes of the present invention can advantageously be coated from water, thus eliminating limitations associated with solvent coating. Furthermore, the combination of surfactant and stabilizer as used in the present invention produces microspheres that are essentially all solid (meth)acrylate microspheres, although there may be a detectable number of hollow or hollow-appearing microspheres, without indications of coagulation or agglomeration during the suspension polymerization process. Depending on the comonomers selected and the reaction/polymerization conditions, the microspheres may be up to 90-95% solvent soluble. Further, depending on the combination of comonomers, surfactant and stabilizer the microspheres are water dispersible, that is, the microspheres can be diluted with water and formulated with water soluble material, but once dried do not redisperse in water.

The microsphere-containing adhesives of the present invention advantageously exhibit improved release characteristics (higher adhesion without fiber pick-up), excellent anchorage to a coated substrate, excellent adhesion to various surfaces (textured surfaces, glass, vinyl), and improved shear holding (hang adhesion). All the improved characteristics are achievable without losing a soft, smooth removal, that is, a non-raspy removal.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The microspheres obtained in the present invention are the reaction product of (i) at least one alkyl (meth)acrylate ester wherein the alkyl group contains four to about 14 carbon atoms, preferably four to about 10 carbon atoms, and (ii) a polar comonomer which, if it comprises dissociable proton, has no dissociable proton having a K_a of greater than 10^{-3} , preferably no greater than 10^{-4} .

Useful alkyl (meth)acrylate monomers are those monofunctional unsaturated (meth)acrylate esters, the alkyl groups of which have from 4 to 14 carbon atoms. Such (meth)acrylates are oleophilic, water dispersible, and are essentially water insoluble. Furthermore, useful (meth)acrylates are those that as homopolymers, generally have a glass transition temperature below about -20°C ., or if a combination of monomers is used, such combination would produce a copolymer or terpolymer generally having a glass transition temperature below about -20°C . Nonlimiting examples of such (meth)acrylates included but are not limited to, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, t-butyl acrylate, t-butyl methacrylate, isobornyl acrylate, methylmethacrylate, isononyl acrylate, isodecyl acrylate and the like, and combination thereof.

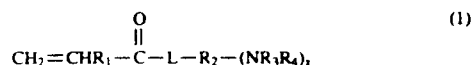
Preferred alkyl (meth)acrylate monomers include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate and mixtures thereof.

Suitable polar comonomers may or may not contain a dissociable hydrogen. In any case, the polar comonomer is one that exhibits a balance of solubility properties in the alkyl (meth)acrylate monomer and water phases of the dispersion obtained when the alkyl (meth)acrylate monomer

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is dispersed in water to provide a significant amount of polar comonomer at or near the interfaces of the two phases, that is, differential solubility of the polar comonomer tends to result in a higher polymerizable concentration at or near the surface of the alkyl (meth)acrylate monomer droplet. Inclusion of the polar comonomer provides microspheres that generally exhibit less tendency to transfer to substrates to which adhesive-coated sheet materials of the invention have been adhered.

One class of suitable polar comonomers having no dissociable proton are amino-functional monomers having a nucleus or portion of the nucleus of the general formula (1):



wherein

R_1 is H, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, cyano or carboxymethyl;

R_2 is a hydrocarbyl radical comprising 1 to about 4 carbon atoms;

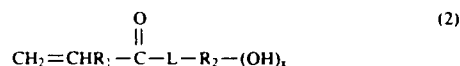
R_3 and R_4 are independently H or an alkyl group containing 1 to about 4 carbon atoms or an arylalkyl group or together form a cyclic or heterocyclic moiety, with the proviso that R_3 and R_4 together do not exceed a total of 8 carbon atoms;

L is a carbon-carbon bond, O, NH or S; and

x is an integer of 1 to 3.

Nonlimiting examples of comonomers of formula 1 include N,N-dimethyl-aminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, t-butylaminoethyl(meth)acrylate and N,N-diethylaminoacrylate.

Another class of suitable polar comonomers having no dissociable proton are hydroxylic comonomers having a nucleus or portion of the nucleus of the general formula (2):



wherein

R_1 is H, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, cyano or carboxymethyl;

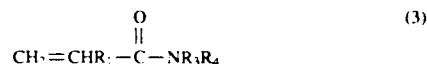
R_2 is a hydrocarbyl radical comprising 1 to about 4 carbon atoms;

L is a carbon-carbon bond, O, NH or S; and

x is an integer of 1 to 3.

Nonlimiting examples of polar comonomers of formula 2 include hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, glycerol mono(meth)acrylate and 4-hydroxybutyl (meth)acrylate.

Yet another class of suitable polar comonomers having no dissociable proton are amido-functional monomers having a nucleus or portion of the nucleus of the general formula (3):



wherein

R_1 is H, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, cyano or carboxymethyl; and

R_3 and R_4 are independently H or an alkyl group containing 1 to about 4 carbon atoms or an arylalkyl group or together form a cyclic or heterocyclic moiety, with the proviso that R_3 and R_4 together do not exceed a total of 8 carbon atoms.

Nonlimiting examples of polar comonomers of formula 3 include N-vinyl pyrrolidone, N-vinyl caprolactam, acrylamide or N,N-dimethyl acrylamide.

Nonlimiting examples of other suitable polar comonomers that do not fall within the above classes and have no dissociable proton include (meth)acrylonitrile, furfuryl

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(meth)acrylate and tetrahydrofurfuryl (meth)acrylate, 2-vinyl pyridine, and 4-vinyl pyridine.

Suitable polar monomers having a dissociable proton are organic carboxylic acids comprising three to about 8 carbon atoms and having generally one to about 4 carboxylic acid moieties. Nonlimiting examples of polar monomers that comprise a dissociable proton, but not a dissociable hydrogen having a K_a of greater than about 10^{-3} include acrylic acid, methacrylic acid, itaconic acid, fumaric acid and crotonic acid.

Generally, the relative amounts by weight of the alkyl (meth)acrylate monomer(s) and the polar comonomer used will be about 99.5/0.5 to 85/15, and will preferably be 98/2 to 92/8.

The microsphere adhesive composition may also contain a crosslinking agent. Examples of useful crosslinking agents include, but are not limited to: multifunctional (meth)acrylate(s), e.g., butanediol diacrylate or hexanediol diacrylate or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof. When used, crosslinker(s) is (are) added at a level of up to about 0.15 equivalent weight percent, preferably up to about 0.1 equivalent weight percent, of the total polymerizable composition.

The microspheres of the present invention are prepared by suspension polymerization using either a one-step or two-step process as described in detail below. Suspension polymerization is a procedure wherein a monomer is dispersed in a medium (usually aqueous) in which it is insoluble. The polymerization is allowed to proceed within the individual polymer droplets. Monomer soluble free-radical initiators are used. The kinetics and the mechanism are essentially those for the corresponding bulk polymerization under the same conditions of temperature and initiator concentration.

Initiators effecting polymerization are those that are normally suitable for free-radical polymerization of acrylate monomers. Examples of such initiators include thermally-activated initiators such as azo compounds, hydroperoxides, peroxides and the like and photoinitiators such as benzophenone, benzoin ethyl ether and 2,2-dimethoxy-2-phenyl acetophenone. Other suitable initiators include lauroyl peroxide and bis(t-butyl cyclohexyl)peroxy dicarbonate. The initiator is present in a catalytically effect amount sufficient to bring about complete monomer conversion in a predetermined time span and temperature range.

Parameters that affect the concentration of initiator employed include the type of initiator and particular monomer and/or monomers involved. It is believed that catalytically effective concentrations range from about 0.10 to about 1 percent by weight of the total monomers and more preferably, from about 0.25 to about 0.70 percent by weight monomers and/or monomers.

A polymeric stabilizer is also utilized. Advantageously, the presence of the stabilizer permits use of relatively low amounts of surfactant while still obtaining desirable solid microspheres. Minimization of the amount of surfactant and the relatively low amount of polymeric stabilizer employed desirably permits the ability of coating the aqueous dispersion of finished microspheres directly onto a backing to obtain an adhesive-coated sheet material exhibiting desirable adhesive properties.

Preferred polymeric stabilizers that assist in the preparation of the microspheres typically have an interfacial tension sufficient to stabilize final polymerized droplets and prevent agglomeration. Interfacial tension herein means the value determined between the monomer phase and a 1.0 percent by weight aqueous solution of the stabilizer and such interfacial tensions are generally above about 15.0 dynes per centimeter.

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Exemplary stabilizers include salts of polyacrylic acids of greater than 5000 molecular weight (e.g., the ammonium, sodium, lithium and potassium salts), carboxy modified polyacrylamides (e.g., Cyanamer™ A-370 from American Cyanamid), copolymers of acrylic acid and dimethylaminoethylmethacrylate and the like, quaternary amines (e.g., General Analine and Film's Gafquat™ 755, a quaternized polyvinyl-pyrrolidone copolymer, or Union Carbide's "JR-400", a quaternized amine substituted cellulosic), and carboxy modified cellulose (e.g., Hercules' Natrosol™ CMC Type 7L, sodium carboxy methylcellulose).

Generally, the polymeric stabilizer will be present in the reaction mixture in an amount by weight of about 0.1 to about 3 parts by weight per 100 parts of polymerizable monomer, and more preferably will be present in an amount by weight of about 0.5 to about 1.5 parts by weight per 100 parts of polymerizable monomer. Polymeric stabilizers can be added to the reaction mixture either singly or as mixture of several stabilizers, the amount of which does not exceed that of a single stabilizer.

In addition, a surfactant is utilized in a concentration greater than the critical micelle concentration (CMC) which is defined as that minimum concentration that is necessary for micelle formation. This concentration can vary with each emulsifier. Generally, the surfactants will be present in the reaction mixture in an amount by weight of no greater than 5 parts by weight per 100 parts by weight of polymerizable monomer, preferably no greater than 3 parts by weight, and most preferably in the range of 0.1 to 1.5 parts by weight per 100 parts by weight of polymerizable monomer. Surfactants can be added to the reaction mixture either singly or as mixture of several surfactants, the amount of which does not exceed that of a single surfactant.

Useful surfactants include anionic, cationic or nonionic surfactants and included but are not limited to anionic surfactants, such as alkyl aryl sulfonates, for example sodium dodecylbenzene sulfonate and sodium decylbenzene, sodium and ammonium salts of alkyl sulfates, for example sodium lauryl sulfate, and ammonium lauryl sulfate; nonionic surfactants, such as ethoxylated oleyl alcohol and polyoxyethylene octylphenyl ether; and cationic surfactants, such as a mixture of alkyl dimethylbenzyl ammonium chlorides wherein the alkyl chain contains from 10 to 18 carbon atoms. Amphoteric emulsifiers are also useful in the present invention and include for example betaine derivatives, sulfobetaine derivatives, N-fatty aminopropionate, N-fatty aminobutyrate, alkyl imidazoline and mixtures thereof.

To initiate the polymerization reaction, a sufficient number of free radicals must be present. This may be achieved through several means that are well known in the art, such as heat or radiation free-radical initiation. For example, heat or radiation can be applied to initiate the polymerization of the monomers, which is an exothermic reaction. However, it is preferred to apply heat until thermal decomposition of the initiators generates a sufficient number of free radicals to begin the reaction. The temperature at which this occurs varies greatly depending upon the initiator used.

In addition, deoxygenation of the polymerization reaction mixture is often desirable. It is well known that oxygen dissolved in the reaction mixture can inhibit polymerization and it is desirable to expel this dissolved oxygen. Although, an inert gas bubbled into the reaction vessel or through the reaction mixture is an effective means of deoxygenation, other techniques for deoxygenation that are compatible with suspension polymerization can be used. Typically, nitrogen is used to deoxygenate, although any of the Group VIIIA

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(CAS version) inert gases, or carbon dioxide are also suitable.

While specific time and stirring speed parameters are dependent upon monomers, initiators, it is desirable to predisperse the reaction mixture until the reaction mixture reaches a state where the average monomer droplet size is between about 5 μm and 80 μm and preferably between 30 μm and 60 μm . The average particle size decreases with increased and prolonged agitation of the reaction mixture.

The stirring and the nitrogen purge are maintained throughout the reaction period. Initiation is begun by heating the reaction mixture. Following polymerization, the reaction mixture is cooled.

In the one-step process both the alkyl (meth)acrylate monomer and the polar comonomer are present together in the suspension at the initiation of polymerization. In the two-step process the polar comonomer is typically added after the initial exotherm resulting from polymerization of the alkyl (meth)acrylate monomer has peaked, but could be added at any point after polymerization has started.

Following polymerization, a stable aqueous suspension of microspheres at room temperature is obtained. The suspension may have non-volatile solids contents of from about 10 to about 60 percent by weight. Upon prolonged standing, the suspension typically separates into two phases, one phase being aqueous and essentially free of polymer and the other phase being an aqueous suspension of the polymeric microspheres, that is, the microsphere-rich phase. The aqueous suspension of microspheres may be utilized immediately following polymerization, because the suspension of microspheres of the present invention is particularly stable to agglomeration or coagulation under room temperature conditions. Advantageously, the microspheres of the present invention can be easily coated from an aqueous solution. Surprisingly, the microspheres of the present invention are well suited for conventional coating techniques and have enhanced fluid processing characteristics.

Separation of the microsphere-rich phase provides an aqueous suspension having a non-volatile solids content, which if diluted with an additional amount of water, will readily redisperse upon shaking or other means of agitation. Generally, this aqueous suspension can be coated onto a backing or other substrate being employed using conventional coating methods, such as slot die coating to provide an adhesive coating. The adhesive coating which, when dried, preferably exhibits a dry coating weight in the range of 0.4 to about 2 grams per square foot to provide an adhesive-coated sheet material in which the adhesive coating comprises polymeric microspheres, polymeric stabilizer and surfactant. Alternatively, the microspheres may be isolated in an organic solvent if desired prior to coating them onto the backing.

Properties of the pressure-sensitive adhesives of the present invention can be altered by the addition of a tackifying resin(s) and/or plasticizer(s). Preferred tackifiers for use herein include hydrogenated rosin esters commercially available from such companies as Hercules, Inc. under the tradenames of ForalTM and PentalynTM. Tackifying resins also include those based on t-butyl styrene. Useful plasticizers include but are not limited to dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate and the like. If such tackifiers and/or plasticizers are used, the amounts used in the adhesive mixture are amounts effective for the known uses of such additives.

Optionally, adjuvants, such as, colorants, fillers, stabilizers, pressure-sensitive latex binders and various other polymeric additives can be utilized. If such adjuvants are used,

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the amounts used in the adhesive mixture are amounts effective for the known uses of such adjuvants.

Suitable backing or substrate materials for use in the present invention include, but are not limited to, paper, plastic films, cellulose acetate, ethyl cellulose, woven or nonwoven fabric formed of synthetic or natural materials, metal, metallized polymeric film, ceramic sheet material and the like. Generally the backing or substrate material is about 50 μm to about 155 μm in thickness, although thicker and thinner backing or substrate materials are not precluded.

The present invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All materials are commercially available or known to those skilled in the art unless otherwise stated or apparent. The following examples are illustrative in nature and are not intended to limit the invention in any way.

TEST METHODS

Static Shear Hold

Static shear hold is determined as the hanging time for an adhesive coated substrate applied to a stainless steel plate when a weight is attached. The procedure followed is:

A 1x1/2 inch (2.5x3.8 cm) sample of the adhesive coated substrate is adhered to a polished steel plate with a 4.5 pound (2 kg) roller. The plate is hung vertically and a 1 kg weight is attached to the free end of the adhesive stripe. A timer is started and the length of time for the adhesive coated sample to release and fall from the steel plate is measured in minutes.

Peel Adhesion

Peel adhesion is the force required to remove a polyester film applied to the coated test material measured at a specific angle and rate of removal. In the examples, this force is expressed in grams per 1.25 inches (3.2 cm) width of coated sheet. The procedure followed is:

A strip, 1.25 inches (3.2 cm) wide, of polyester film is applied to the horizontal surface of a coated sample fixed on a test plate. A 4.5 lb. (2 kg) hard rubber roller is used to apply the strip. The free end of the polyester film is attached to the adhesion tester load cell so that the angle of removal will be 90 degrees. The test plate is then clamped in the jaws of the tensile testing machine that is capable of moving the plate away from the load cell at a constant rate of 12 inches (31 cm) per minute. A load cell reading in grams per 1.25 inches (3.2 cm) of coated strip is recorded as the polyester film is peeled from the coated samples. The samples are tested three times. The average of the three tests is reported below.

Microsphere Transfer

Microsphere transfer for the purposes of this test is defined as the amount of microsphere that transfers to an applied paper when the coated sample is removed from the paper. It is measured as the percent of the area covered with microspheres. The procedure followed is:

A three-quarter (3/4) (1.9 cm) wide strip of microsphere coated sample is adhered to a clean area of a clay coated paper commercially available as Kromcoat, for a few seconds using the mechanical rolling action provided by an TLMI release and adhesion tester and then is removed at a 90° degree angle at a constant rate. The clay coated strip is then surveyed by an image processor through a video camera and the percent microsphere coverage of the viewed area is recorded. Ten fields were surveyed on each test sample and the average of these readings is recorded.

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Glossary

AA—acrylic acid
 ACM—acrylamide
 CRA—crotonic acid
 FA—fumaric acid
 HEMA—hydroxyethyl methacrylate
 IOA—isoctyl acrylate
 IPA—isopropyl alcohol
 ITA—itaconic acid
 NVP—N-vinyl pyrrolidone

EXAMPLES

Example 1

To a 2 liter, 3 necked flask equipped with thermometer, reflux condenser, mechanical stirrer and nitrogen inlet tube, were charged 739 grams of deionized water, and 9.6 grams of Acrysol™ A3 (tradename for a 25 percent solids aqueous solution of polyacrylic acid of 190,000 molecular weight, commercially available from the Rohm and Haas Company) and 10 grams of Triton™ X 200 (tradename for a 28% solids aqueous suspension of sodium alkylaryl polyether sulfonate, commercially available from Rohm and Haas Company). The contents of the flask were then agitated and concentrated ammonium hydroxide was added there to until a pH of 7.0 was obtained and heated 70° C. To this solution were added 239 grams of isoctylacrylate and 0.8 grams of Perkadox™ 16N (tradename for a 94.5% active BIS (4-tert-butyl cyclohexyl) peroxydicarbonate initiator commercially available from AKZO Chemicals, Inc. The agitation was set at 600 revolutions per minute (rpm) and the reaction mixture was purged with nitrogen. The stirring and nitrogen purge were maintained throughout the reaction period. The reaction mixture was maintained at 65° C. to initiate the reaction. The reaction became exothermic after a few minutes of heating. After the exotherm had peaked (80° C.), 14.8 grams of acrylic acid was added slowly to the reaction flask and the batch was heated to 90° C. for two hours. The reaction mixture was then cooled to room temperature and filtered through a cheese cloth. Very little coagulum was observed to be present.

The vinylic moiety, the amount of vinylic moiety, the peel adhesion, and the microsphere transfer are summarized in Table 1.

Example 2-5

Examples 2-5 illustrate the use of various vinylic moieties. The microspheres of these Examples were prepared in accordance with the procedures outlined in Example 1. The vinylic moiety, the amount of vinylic moiety, the peel adhesion, and the microsphere transfer are summarized in Table 1.

Comparative Example C1

Comparative Example C1 was prepared in accordance with the procedures outlined in Example 1 except that no acrylic acid was added after exotherm.

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The test results are reported in Table 1.

TABLE 1

| Ex | Monomer | Vinylic Moiey (gm) | Peel Adhesion (g/1.25 in.) | Microsphere Transfer |
|----|---------|--------------------|----------------------------|----------------------|
| 1 | AA | 14.8g | 117.1 | 6.9 |
| 2 | HEM | 19.0g | 75.2 | 1.2 |
| 3 | NVP | 19.0g | 89.4 | 1.09 |
| 4 | AcM | 19.0g | 84.5 | 1.3 |
| 5 | AA/Acm | 9.5/9.5 | 88.5 | 0.30 |
| C1 | — | — | 66.8 | 30.0 |

Example 6

To a two liter, 3-necked flask equipped with a thermometer, mechanical stirrer and nitrogen inlet tube, was charged 650 grams of deionized water, 5.8 gm of Triton™ X 200 (tradename for 28% solids aqueous suspension of sodium alkyl arylpolyether sulfonate commercially available from Rohm and Haas Company), 14 gm of Acumer™ IS-30 (tradename for a 25 percent solids aqueous solution of polyacrylic acid of 190,000 molecular weight, commercially available from Rohm and Haas Company), 2.8 gm of concentrated ammonium hydroxide (a stoichiometric amount of base to give ammonium polyacrylate), and 14 gms of acrylic acid. To this solution was added 350 gms of isoctylacrylate and 1.1 gms of Perkadox™ 16N (tradename for a 95% active bis(4-tert-butylcyclohexyl) peroxydicarbonate initiator commercially available from AKZO Chemicals, Inc.). The agitation was set at 450 revolutions per minute (RPM) and the reaction mixture was heated to 45° C. and purged with nitrogen. The stirring, nitrogen purge and temperature was maintained throughout the reaction period, the reaction was exothermic after a few minutes and peaked at 69° C. The batch was maintained at 45° C. for two more hours, cooled, and filtered through cheese cloth. Very little coagulum was found to be present. The resulting suspension was found to contain microspheres of an average particle size of 77.6 microns which on creaming had a lower phase solids of 2% by weight. Microscopic examination showed the microsphere to be a solid sphere.

Examples 7-20

Examples 7-20 included in Table 2 below illustrate the use of various polar vinylic monomers, stabilizers or surfactants. The microspheres of these examples were prepared in accordance with the procedures outlined in Example 6. The polar monomer, surfactant type, and stabilizer type along with the particle size, coagulum and lower phase solids are also reported. The data shows that at relatively low concentrations of surfactant (0.5% of monomer concentration) stable microsphere dispersions can be made with the addition of a stabilizer and a polar vinylic comonomer.

Comparative Example C2

Comparative Example C2 was prepared in accordance with the procedure described in Example 7, except no stabilizer was added to the reaction mixture. The results are summarized in Table 2 and indicate that without the stabilizer, the reaction mixture coagulates.

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Comparative Example C3

Comparative Example C3 was prepared in accordance with Example 18, except no comonomer was added in the

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reaction mixture. The results are summarized in Table 2 and indicates that without the comonomer, the reaction mixture coagulates.

TABLE 2

| Sample No. | Surfactant | Stabilizer | Comonomer | Initiator | Coagulum (% by weight) | Particle Size (micrometer) | Lower Phase Solids (% by weight) |
|------------|-------------------------------------|---|--|-------------------------------|------------------------|----------------------------|----------------------------------|
| 6 | 5.8 gm Triton™ X200 | 14 gm Acumer™ 15-30 (Neutralized) | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | None | 77.6 | 2.0 |
| 7 | 3.5 gm Polystep™ LAS50 ¹ | 7 gm Acumer™ 15-30 (Neutralized) | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | None | 44.6 | 1.0 |
| 8 | 5.8 gm Polystep™ B7 ² | 7 gm Acumer™ 15-30 (Neutralized) | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | None | 46.5 | 1.1 |
| 9 | 5.8 gm Polystep™ B5 ³ | 7 gm Acumer™ 15-30 (Neutralized) | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | None | 47.5 | 1.0 |
| 10 | 1.8 gm Polystep™ A13 ⁴ | 7 gm Acumer™ 15-30 (Neutralized) | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | None | 55.8 | 1.1 |
| 11 | 1.8 gm Siponate™ DS10 ⁵ | 11.5 gm polyacrylamide (High Carboxyl) ⁶ | 14 gm hydroxy ethyl methacrylate | 1.1 gm Perkadox™ 16 | None | 47.9 | 1.6 |
| 12 | 6.2 gm Stephanol™ AM ⁶ | 23 gm polyacrylamide (High Carboxyl) ⁶ | 3.5 gm acrylic acid | 1.4 gm benzoyl peroxide (70%) | 2% | 38.5 | 5.5 |
| 13 | 1.8 gm Siponate™ DS10 ⁵ | 7 gm Goodrite™ K702 (Neutralized) ⁷ | 14 gm N-vinyl pyrrolidone | 1.1 gm Perkadox™ 16 | 1% | 54.4 | 0.9 |
| 14 | 3.8 gm Stephanol™ AM ⁶ | 7 gm Goodrite™ K702 (Neutralized) ⁷ | 14 gm N-vinyl caprolactam | 1.1 gm Perkadox™ 16 | 0.5% | 46.5 | 1.5 |
| 15 | 5.8 gm Triton™ X200 | 11.5 gm polyacrylamide (High Carboxyl) ⁶ | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | 1% | 78.7 | 1.4 |
| 16 | 6.2 gm Stephanol™ AM ⁶ | 14 gm Goodrite™ K702 (Neutralized) ⁷ | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | 2% | 48.0 | 2.7 |
| 17 | 6.2 gm Stephanol™ AM ⁶ | 23 gm polyacrylamide (High Carboxyl) ⁶ | 14 gm acrylic acid | 1.4 gm benzoyl peroxide (70%) | 2% | 49.2 | 4.2 |
| 18 | 6.2 gm Stephanol™ AM ⁶ | 7 gm Goodrite™ K702 (Neutralized) ⁷ | 14 gm hydroxy ethyl methacrylate | 1.1 gm Perkadox™ 16 | 0.50% | 57.3 | 1.5 |
| 19 | 6.2 gm Stephanol™ AM ⁶ | 7 gm Goodrite™ K702 (Neutralized) ⁷ | 14 gm N-vinyl pyrrolidone | 1.1 gm Perkadox™ 16 | None | 71.4 | 1.4 |
| 20 | 6.2 gm Stephanol™ AM ⁶ | 14 gm Goodrite™ K702 (Neutralized) ⁷ | 3.5 gm acrylic acid and 10.5 gm acrylamide | 1.1 gm Perkadox™ 16 | 2% | 51.8 | 3.7 |
| C2 | 3.5 gm Polystep™ LAS50 ¹ | None | 14 gm acrylic acid | 1.1 gm Perkadox™ 16 | 100% | NA | NA |
| C3 | 6.2 gm Stephanol™ AM ⁶ | 7 gm Goodrite™ K702 (Neutralized) ⁷ | None | 1.1 gm Perkadox™ 16 | 100% | NA | NA |

¹Polystep™ LAS50 is a 50% solids solution of sodium dodecyl benzene sulfonate commercially available from Stepan Company.

²Polystep™ B7 is a 30% solids solution of ammonium lauryl sulfate commercially available from Stepan Company.

³Polystep™ B5 is a 30% solids solution of sodium lauryl sulfate commercially available from Stepan Company.

⁴Polystep™ A13 is a 97% active linear dodecylbenzene sulfonic acid commercially available from Stepan Company (neutralized with ammonia).

⁵Siponate™ DS10 is flakes of sodium dodecyl benzene sulfonate commercially available from Alcolac Inc.

⁶Stepanol™ AM is a 29% solids solution of ammonium lauryl sulfate commercially available from Stepan Company.

⁷Goodrite™ K702 is a 25% solids solution of polyacrylic acid commercially available from BF Goodrich Company.

⁸This is a 15% solids solution of polyacrylamide (high carboxyl modified) commercially available from Aldrich Chemical (neutralized with ammonia).

Example 21

To a 2 liter, 3 necked flask equipped with thermometer, reflux condenser, mechanical stirrer and nitrogen inlet tube were charged 650 gm of deionized water, and 7 gm of Goodrite™ K702 (tradename for a 25% solids aqueous solution of polyacrylic acid of 240,000 molecular weight, commercially available from B.F. Goodrich Company) and 1.8 gms of Siponate™ DS10 (tradename for sodium dode-

cylbenzene sulfonate, commercially available from Alcolac, Inc.) The contents of the flask were then agitated and concentrated ammonium hydroxide was added thereto until a pH of 7.0 was obtained. The flask was heated to 50° C. and 14 gms of N-vinylpyrrolidone, 1.1 gms of Perkadox™ 16N (tradename for 94.5% active bis-(4-tert-butyl cyclohexyl) peroxydicarbonate initiator commercially available from AKZO Chemical Inc.), and 350 gms of isooctylacrylate were added and the agitation was set at 410 rpm. The

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reaction mixture was purged with nitrogen and became exothermic after a few minutes of heating. The 50° C. batch temperature was maintained for five hours and the mixture cooled to room temperature and filtered through cheese cloth. Very little coagulation was observed and the resulting suspension was found to contain microspheres of an average particle size of 40.5 microns. This suspension was made into a coating by adding 153 gms to 13 gms of the suspension of an isooctylacrylate/acrylic acid copolymer latex (monomer ratio was 96/4) and 3 gms of Acrysol™ ASE95 (an 18% solids acrylic thickener commercially available from Rohm and Haas Company) and 32 gms of water. This coating was mixed and neutralized with concentrated ammonium hydroxide to pH 7.0 and coated on a primed backing of bond paper at a rate of 0.8 gm/sq. ft. The results are tabulated in Table 3 below.

TABLE 3

| | |
|--|-------------|
| Peel adhesion to polyester (grams/1.25 inches) | 125.1 |
| Peel adhesion to bond paper (grams/inch) | 93.4 |
| Percent microsphere transfer | 0.8% |
| Static shear hold | 653 minutes |

Examples 22-24

Examples 22-24 illustrate the improvement in anchorage by increasing the amount of acrylic acid in the microspheres. These were prepared according the procedure described in Example 18 and were made into a coating with 4% of an acrylate terpolymer latex containing an N-alkyl substituted acrylamide available from BF Goodrich under the tradename of Hycar™ 2600x222 and 1% of an acid containing acrylic emulsion copolymer thickener available from Rohm and Haas Co. under the tradename Acrysol™ ASE 95 NP. The coatings were applied to a primed bond paper using coating procedures known in the art. The test results are summarized in Table 4.

Comparative Examples C4 (a) and (b)

Comparative Examples C4 (a) and (b) were prepared according to the procedure described in Examples 17-19, except there was no acrylic acid added. To prepared a microsphere suspension that did not coagulate and was coatable, sodium propionate and ethylene amine hydrochloride were added in place of the co-monomer (C4 (a)) and (C4 (b)), respectively.

TABLE 4

| Example | Microsphere IOA/AA Ratio | Peel Adhesion (gm/1.25") to polyester film | Percent Microsphere Transfer |
|---------|--------------------------|--|------------------------------|
| C4 (a) | 100 | 66.3 | 25.9 |
| C4 (b) | 100 | 71.0 | 26.4 |
| 22 | 99.5/0.5 | 93.6 | 21.7 |
| 23 | 99.0/1.0 | 91.6 | 4.2 |
| 24 | 96.0/4.0 | 92.0 | 0.1 |

The data shows a decrease in transfer as the percent of acrylic acid increases.

Examples 25-27

Examples 25-27 illustrate the build of adhesion on aging using different polar comonomers. These examples were prepared using the procedure described in Example 18 and using techniques known to those skilled in the art.

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Peel adhesions were measured according to the above-described procedures. The test results are summarized in Table 5.

TABLE 5

| Example | % Polar Comonomer | Peel Adhesion (gm/inch) | | | |
|---------|--------------------|-------------------------|----------------------|---------------|-----------------------|
| | | Bond Initial | Bond 3-days humidity | Vinyl Initial | Vinyl 3-days humidity |
| 25 | 4% AA | 98.1 | 202.8 | 108.9 | 36.6 |
| 26 | 4% HEMA/ 1% AA | 120.9 | 161.9 | 114.5 | 48.5 |
| 27 | 4% NVP/ 0.5% AA | 113.6 | 181.5 | 132.8 | 233.8 |

The data shows an increase in the adhesion on aging with acrylic acid MSA against bond paper and a decrease in adhesion when aged against a vinyl notebook. However, N-vinyl pyrrolidone microspheres show a significant increase in adhesion to vinyl on aging at high humidity (80% RH at 70° F.).

Examples 28-30

Examples 28-30 illustrate the effect of polar comonomer in isooctylacrylate microspheres when hanging on a vertical surface, such as a painted metal. The samples were prepared as described in Example 18 and were cut to apply a 1"x1.5" (2.5x3.8 cm) area of adhesive coated paper to the metal surface. The paper was then hung vertically with a 1 kg weight attached to the paper extending from the edge of the painted metal. The time before shear failure was then recorded. The results are summarized in Table 6.

TABLE 6

| Example | % Polar Comonomer | Static Shear Hold Time to Painted Metal (min) |
|---------|-------------------|---|
| 28 | 4% AA | 34.4 |
| 29 | 4% HEMA/1% AA | 20.2 |
| 30 | 4% NVP/0.5% AA | 194.5 |

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention is not be unduly limited to the illustrative embodiments set forth hereinabove. All publications and patents are incorporated herein by reference to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference.

We claim:

1. A sheet material comprising a backing and a coating of repositionable pressure-sensitive adhesive coated on at least one major surface of said backing, the adhesive comprising:

- i) a plurality of polymeric, solid, elastomeric microspheres that are the reaction product of reactants comprising polymerizable starting materials comprising at least one C₄-C₁₄ alkyl (meth)acrylate monomer and at least one polar comonomer with the proviso that if the polar comonomer comprises a dissociable proton, the polar comonomer has no dissociable proton having a K_a of greater than 10⁻³;
- ii) a polymeric stabilizer in an amount of about 0.1 to about 3 parts by weight per 100 parts by weight of the microspheres; and

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iii) a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of the microspheres.

2. A sheet material according to claim 1, wherein the alkyl (meth)acrylate is selected from the group consisting of isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, and isodecyl acrylate.

3. A sheet material according to claim 1, wherein the polar comonomer is selected from the group consisting of acrylic acid, N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl pyridine, methacrylic acid, acrylamide, fumaric acid, itaconic acid, crotonic acid, acrylonitrile, methacrylonitrile, hydroxyethylacrylate, and hydroxyethyl methacrylate.

4. A sheet material according to claim 1, wherein the polymeric stabilizer is a salt of polyacrylic acid.

5. A sheet material according to claim 1, wherein the polymeric stabilizer is present in an amount of about 0.5 to about 2 parts by weight per 100 parts by weight of the microspheres.

6. A sheet material according to claim 1, wherein the surfactant is ammonium lauryl sulfate.

7. A sheet material according to claim 1, wherein the surfactant is present in an amount of no greater than 5 parts by weight per 100 parts by weight of the microspheres.

8. A sheet material according to claim 1, wherein the dry coating weight of adhesive is in the range of 0.4 to about 2 gms per square foot of surface area of the sheet material.

9. A sheet material according to claim 1, wherein the backing is about 2 to about 6 mils in thickness.

10. The sheet material according to claim 1 comprising a backing and a coating of repositionable pressure-sensitive adhesive coated on at least one major surface of said backing, the coating comprising a plurality of microspheres prepared according to the following process:

- a) stirring or agitating a mixture comprising polymerizable monomer starting materials comprising (1) at least one C_1 - C_{14} alkyl (meth)acrylate monomer; (2) a polar comonomer which, when the polar comonomer comprises a dissociable proton, has no dissociable proton

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having a K_a greater than 10^{-3} , (3) a catalytically effective amount of an initiator for the polymerizable monomer starting materials; (4) a polymeric stabilizer in an amount of about 0.1 to about 3 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; (5) a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; and (6) water to form an oil in water suspension; and

- b) polymerizing the polymerizable monomer starting materials, wherein the microspheres are provided.

11. The sheet material according to claim 1 comprising a backing and a coating of repositionable pressure-sensitive adhesive coated on at least one major surface of said backing, the coating comprising a plurality of microspheres prepared by the following process:

- a) stirring or agitating a mixture comprising a polymerizable monomer starting materials comprising (1) at least one C_1 - C_{14} alkyl (meth)acrylate monomer; (2) a catalytically effective amount of an initiator for the polymerizable monomer starting materials; (3) a polymeric stabilizer in an amount of about 0.1 to about 3 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; (4) a surfactant in an amount of no greater than about 5 parts by weight per 100 parts by weight of the polymerizable monomer starting materials; and (5) water to form an oil in water suspension; and
- b) at least partially polymerizing the polymerizable monomer starting materials;
- c) adding to the suspension a polar comonomer which, when the polar comonomer comprises a dissociable proton, has no dissociable proton having a K_a greater than 10^{-3} ; and
- d) continuing the polymerization of the polymerizable monomer starting materials, wherein microspheres are provided.

* * * * *

United States Patent [19]
Delgado

[11] Patent Number: 4,968,562
 [45] Date of Patent: Nov. 6, 1990

[54] **HOLLOW ACID-FREE ACRYLATE
 POLYMERIC MICROSPHERES HAVING
 MULTIPLE SMALL VOIDS**

[75] Inventor: **Joaquin Delgado, St. Paul, Minn.**

[73] Assignee: **Minnesota Mining and
 Manufacturing Company, St. Paul,
 Minn.**

[21] Appl. No.: 485,630

[22] Filed: Feb. 27, 1990

[51] Int. Cl.³ B32B 5/16

[52] U.S. Cl. 428/402; 521/56;
 521/60; 521/63; 521/64; 523/223; 524/801

[58] Field of Search 428/402; 524/801;
 523/223; 521/56, 60, 63, 64

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| 3,691,140 | 9/1972 | Silver | 260/78.5 |
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| 4,166,152 | 8/1979 | Baker et al. | 428/522 |
| 4,495,318 | 1/1985 | Howard | 524/375 |
| 4,598,112 | 7/1986 | Howard | 524/78 |
| 4,645,783 | 2/1987 | Kinoshita | 523/221 |
| 4,656,218 | 4/1987 | Kinoshita | 524/460 |
| 4,735,837 | 4/1988 | Miyasaka et al. | 428/40 |
| 4,786,696 | 11/1988 | Bohnel | 526/88 |

FOREIGN PATENT DOCUMENTS

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 Kirn; Darla P. Neaveill

[57] **ABSTRACT**

Hollow, polymeric, acrylate, infusible, inherently tacky, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres having an average diameter of at least about 1 micrometer wherein a majority of the microspheres contain multiple interior voids, a majority of the voids having a diameter of less than about 10% of the diameter of the microspheres, the total of the diameters of the voids being at least about 10% of the diameter of the microsphere.

These hollow microspheres are useful as repositionable pressure-sensitive adhesives. The invention also provides pressure-sensitive adhesives consisting essentially of such acid-free hollow microspheres. Aqueous suspensions of these microspheres, processes for their preparation, spray repositionable pressure-sensitive adhesive compositions, and pressure-sensitive adhesive coated sheet materials are also provided. Surprisingly, hollow microspheres of the invention may be used in combination with delicate substrates such as photographs without causing discoloration or damage, in comparison with prior art repositionable pressure-sensitive adhesives.

14 Claims, No Drawings

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HOLLOW ACID-FREE ACRYLATE POLYMERIC MICROSPHERES HAVING MULTIPLE SMALL VOIDS

FIELD OF THE INVENTION

This invention relates to hollow, polymeric, acrylate, infusible, inherently tacky, elastomeric, solvent-dispersible, solvent-insoluble, nitrogen-containing, acid-free microspheres, to processes for their preparation, and to their use as repositionable pressuresensitive adhesives.

BACKGROUND OF THE INVENTION

Description of the Related Art

Solid, inherently tacky, elastomeric microspheres are known in the art to be useful in repositionable pressure-sensitive adhesive applications. As used herein, the term "repositionable" refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability. Microsphere-based adhesives are thought to perform well in such applications at least in part due to their "self-cleaning" character, wherein substrate contaminants tend to be pushed aside and trapped between the microspheres as the adhesive is applied. Upon removal, the adhesive can then still present a relatively uncontaminated surface for reapplication to the substrate. However, problems with microsphere loss, i.e., microsphere transfer to the substrate, and the resultant need for use of a primer or binder have been recognized in the art.

Numerous references concern the preparation and/or use of inherently tacky, elastomeric acrylate polymeric microspheres which are solid in nature. Such spheres and their use in aerosol adhesive systems having repositionable properties are disclosed in U.S. Pat. No. 3,691,140 (Silver). These microspheres are prepared by aqueous suspension polymerization of alkyl acrylate monomers and ionic comonomers, e.g., sodium methacrylate, in the presence of an emulsifier, preferably an anionic emulsifier. The use of a water-soluble, substantially oil-insoluble ionic comonomer is critical to preventing coagulation or agglomeration of the microspheres.

U.S. Pat. No. 4,166,152 (Baker et al.) describes solid, inherently tacky (meth)acrylate microspheres which are prepared from non-ionic alkyl acrylate or methacrylate monomer(s) in the presence of both an emulsifier and an ionic suspension stabilizer having an interfacial tension sufficient to prevent microsphere agglomeration. Such microspheres are also disclosed in U.S. Pat. Nos. 4,495,318 and 4,598,112 (Howard), where the preparative methods involve the use of a nonionic emulsifier or a cationic emulsifier. All three patents disclose utility as a "reusable adhesive".

U.S. Pat. No. 4,786,696 (Bohnel) describes a suspension polymerization process for preparing solid, inherently tacky (meth)acrylate microspheres which does not require the use of either an ionic comonomer or an ionic suspension stabilizer in order to prevent agglomeration. Rather, the process requires agitation of the vessel charge prior to the initiation of the reaction sufficient to create a suspension of monomer droplets having an average monomer droplet size of between about 5 and about 70 micrometers. In addition to (meth)acrylate monomer, a minor portion of a non-ionic, vinyl'ic comonomer such as, e.g., acrylic acid may be included to modify the "tacky nature" of the microspheres.

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U.S. Pat. No. 3,620,988 (Cohen) discloses a method of preparing "bead-type polymers" which involves the use of a water-insoluble polymeric thickening dispersing agent. The method can be applied to produce coatable bead suspensions which can be formed into continuous films having pressure-sensitive adhesive properties.

U.S. Pat. No. 4,735,837 (Miyasaka et al.) discloses a detachable adhesive sheet having an adhesive layer containing "elastic micro-balls", wherein the microballs partially protrude from the surface of the adhesive layer. The microballs may or may not be tacky. They can be derived from, e.g., (meth)acrylate monomer and an α -olefinic carboxylic acid monomer via suspension polymerization in an aqueous medium. However, no details as to the nature of the surfactants utilized, etc., are disclosed. The microballs and an adhesive are dispersed in solvent, mixed, and coated, with the ratio of adhesive to microballs being from about 1:10 to about 10:1. This ratio is disclosed to be critical in order that all microballs in the final product, including those protruding from the surface, are completely covered with the adhesive. A range of 1,000 to 150,000 pieces per square centimeter is disclosed as preferred.

DE 3,544,882 A1 (Nichiban) describes crosslinked microspheres composed of 90 to 99.5 weight percent of (meth)acrylate ester and 10 to 0.5 weight percent of vinyl type monomer, e.g., acrylic acid, having a reactive functional group through which crosslinking is achieved by reaction with an oil-soluble crosslinking agent. The microspheres are prepared by dispersing in water a solution (in organic solvent) of copolymer prepared by known methods such as solution, bulk, emulsion, or suspension polymerization. (However, the reference notes that in cases where emulsion or suspension polymerization is used with water as a dispersion medium, it is not necessary to make a new aqueous dispersion.) When tacky, the spheres are said to be useful in spray or coated sheet form as "removable adhesive". The stated purpose of the invention is to provide microspheres having a uniform particle size, but it is also stated that the microspheres may contain other monomers such as vinyl acetate, styrene, acrylonitrile, methacrylonitrile, etc., "... to prevent partial transfer of the adhesive when the carrier (backing) is pulled away from the substrate ...".

U.S. Pat. Nos. 4,645,783 and 4,656,218 (Kinoshita) disclose a "repeatedly usable and releasable sheet" coated with an aqueous suspension of microspheres obtained by aqueous suspension polymerization (in the presence of a protective colloid comprising casein as a main ingredient) of one or more alkyl(meth)acrylate esters, one or more α -monoolefin carboxylic acids, and one or more other vinyl monomers. The microspheres are preferably interspersed with finer polymer particles prepared by polymerization of one or more vinyl monomers in an aqueous medium. These fine polymer particles are said to be "... effective in improving the anchorage to the adherend and the adhesion to the substrate after the aqueous suspension prepared in accordance with the present invention is applied to the substrate".

U.S. Pat. No. 3,857,731 (Merrill et al.) and EP 209337 (Smith & McLaurin) both address problems with microsphere adhesive transfer. The former discloses sheets coated with the tacky elastomeric copolymer microspheres of the Silver patent and a binder material which provides sockets in which the microspheres are held by predominately mechanical forces. The latter states that

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microsphere adhesives could be put to more demanding applications if it were not for the drawback of adhesive transfer. Tacky, elastomeric microspheres are then described which have a composition formed from non-ionic monomers alone or together with a proportion of ionic comonomers. The microspheres further comprise an adhesion promoting monomer having functionality which remains unreacted during polymerization of the monomers and is available for subsequently binding the microspheres through electrostatic interaction or chemical bonding to a substrate or binder-coated substrate. Preferably, the microspheres are derived from at least one alkyl acrylate or methacrylate ester.

U.S. Statutory Invention Registration H509 (Chao) discloses acrylate microparticle adhesives wherein the level of tack is varied by adjusting the type and ratio of monomers used in the starting solution. Very high tack is said to be achieved when isodecylacrylate and 2 ethyl hexylacrylate are used in combination with acrylic acid, vinyl pyrrolidone, and isoboryl acrylate.

It is an object of this invention to provide an acid-free microsphere-based, repositionable pressure-sensitive adhesive for use where acids would cause problems with the substrate such as discoloration, i.e., photographs.

It is a further object of this invention to provide an elastomeric microsphere-based, repositionable pressure-sensitive adhesive which exhibits good shear adhesion, enabling the adhesive to support heavy objects.

It has now been discovered that these objects, and others, which will become apparent from the following discussion may be achieved by preparing hollow microspheres having multiple small voids which, in addition to being inherently tacky, elastomeric, infusible, solvent-insoluble, and solvent-dispersible, are also nitrogen-containing and acid-free.

SUMMARY OF THE INVENTION

This invention provides hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, acid-free pressure-sensitive adhesive microspheres having diameters of at least about one micrometer. A majority of the microspheres contain multiple interior voids, a majority of the voids having a diameter of less than about 10% of the diameter of the microsphere, the total of all void diameters being at least about 10% of the diameter of the microsphere. These microspheres are useful as repositionable pressure-sensitive adhesives.

The invention also provides pressure-sensitive adhesives based on the acid-free hollow microspheres, aqueous suspensions of these microspheres, processes for their preparation, spray repositionable pressure-sensitive adhesive compositions, and pressure-sensitive adhesive-coated sheet materials.

Repositionable pressure-sensitive adhesives based on nitrogen-containing, acid-free microspheres having multiple small voids can be used even on such delicate substrates as photographs, graphics, silkscreened printed matter, and the like, which would discolor if used with conventional, acid-containing repositionable pressure-sensitive adhesives.

It has been discovered that increasing the amount of N-containing polar monomer results in higher shear adhesion without detrimental effect on the other pressure-sensitive adhesive properties. Thus, adhesives of the invention comprising higher, i.e., 15-25 parts of the N-containing polar monomer exhibit greater shear ad-

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hesion for a given coating weight of adhesive than prior art systems. The hollow acid-free microspheres of this invention are also highly adherent to substrates on which they are coated, and, thus, generally require neither separate primer or binder material.

This invention also provides a pressure-sensitive adhesive consisting essentially of these nitrogen-containing, acid-free hollow microspheres. More specifically, the pressure-sensitive adhesive consists essentially of hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free microspheres comprising:

(a) at least about 70 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester; and

(b) up to about 30 parts by weight of at least one nitrogen-containing polar monomer, a majority of the microspheres having multiple interior voids, a majority of the voids having a diameter of less than about 10% of the diameter of the microsphere, the total of all void diameters being at least about 10% of the diameter of the microsphere.

These hollow acid-free microspheres may be prepared by a two-step emulsification polymerization process comprising the steps of:

(a) forming a water-in-oil emulsion of an aqueous solution of nitrogen-containing polar monomer(s) in oil phase monomer(s);

(b) forming a water-in-oil-in-water emulsion by dispersing the water-in-oil emulsion into an aqueous phase; and

(c) initiating polymerization preferably by application of heat (or radiation).

Acid-free hollow microspheres may also be prepared by a simpler ("one-step") emulsification process comprising aqueous suspension polymerization of at least one alkyl acrylate or alkyl methacrylate ester monomer and at least one non-ionic nitrogen-containing polar monomer in the presence of at least one emulsifier which is capable of producing a water-in-oil emulsion inside the droplets, as defined below, which is substantially stable during emulsification and polymerization. Both methods produce an aqueous suspension of monomer droplets which upon polymerization become microspheres, a majority of which have multiple interior cavities that, upon drying, become voids.

The following terms have these meanings as used herein:

1. The term "droplet" means the liquid stage of the microspheres prior to the completion of polymerization.

2. The term "cavity" means a space within the walls of a droplet or microsphere when still in the suspension or dispersion medium prior to drying, and thus containing whatever medium was used.

3. The term "void" means an empty space completely within the walls of a polymerized microsphere.

4. The term "hollow" means containing at least one void or cavity.

5. The term "acid-free" means the monomers utilized contain no proton-donating species, specifically no carboxylic or sulphonic acid groups.

All percents, parts, and ratios described herein are by weight unless specifically stated otherwise.

DETAILED DESCRIPTION OF THE INVENTION

Alkyl acrylate or methacrylate monomers useful in preparing the hollow microspheres and pressure-sensi-

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tive adhesives of this invention are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to about 14 carbon atoms. Such acrylates are oleophilic, water emulsifiable, have restricted water solubility, and as homopolymers, generally have glass transition temperatures below about -20°C . Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, and the like, singly or in mixtures.

Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate, and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have glass transition temperatures higher than about -20°C , e.g., tert-butyl acrylate, isobornyl acrylate, butyl methacrylate, vinyl acetate, and the like, may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is below about -20°C . When methacrylate monomer is the sole alkyl acrylate utilized, a crosslinking agent, *infra*, must be included.

Nitrogen-containing polar monomers suitable for copolymerization with the acrylate or methacrylate monomers to produce acid-free hollow microspheres are those nitrogen-containing polar monomers which are both somewhat oil-soluble and water-soluble, resulting in a distribution of the polar monomer between the aqueous and the oil phases.

Representative examples of suitable nitrogen-containing polar monomers include N-vinyl-2-pyrrolidone, N-vinyl caprolactam, 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (vinyl azlactone), acrylamide, t-butyl acrylamide, dimethylaminoethyl methacrylate, and N-octyl acrylamide.

The hollow microspheres of this invention and the pressure-sensitive adhesives made therefrom comprise at least about 70 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester and correspondingly, up to about 30 parts by weight of one or more nitrogen-containing polar monomers. Preferred microspheres contain at least about 85 parts by weight of the alkyl acrylate, and up to about 15 parts by weight of the nitrogen-containing polar monomer. At least one nitrogen-containing polar monomer is included in the composition. For most nitrogen-containing polar monomers, incorporation of from about 1 part to about 15 parts by weight is preferred, as this ratio provides hollow microspheres with balanced pressure-sensitive adhesive properties.

Aqueous suspensions of the hollow microspheres may be prepared by a "two-step" emulsification process which first involves forming a water-in-oil emulsion of an aqueous solution of nitrogen-containing polar monomer(s) in oil phase monomer, i.e., at least one acrylate or methacrylate ester, using an emulsifier having a low hydrophilic-lipophilic balance (HLB) value. Suitable emulsifiers are those having an HLB value below about 7, preferably in the range of about 2 to about 7. Examples of such emulsifiers include sorbitan monooleate, sorbitan trioleate, and ethoxylated oleyl alcohol such as Brij™ 93, available from Atlas Chemical Industries, Inc. Thus, in this first step, oil phase monomer(s), emul-

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sifier, a free radical initiator, and, optionally, a crosslinking monomer or monomers as defined below are combined, and an aqueous solution of all or a portion of the polar monomer(s) is agitated and poured into the oil phase mixture to form a water-in-oil emulsion. A thickening agent, e.g., methyl cellulose may also be included in the aqueous phase of the water-in-oil emulsion. In the second step, a water-in-oil-in-water emulsion is formed by dispersing the water-in-oil emulsion of the first step into an aqueous phase containing an emulsifier having an HLB value above about 6. The aqueous phase may also contain any portion of the polar monomer(s) which was not added in step one. Examples of such emulsifiers include ethoxylated sorbitan monooleate, ethoxylated lauryl alcohol, and alkyl sulfates. In both steps, when an emulsifier is utilized, its concentration should be greater than its critical micelle concentration, which is herein defined as the minimum concentration of emulsifier necessary for the formation of micelles, i.e., submicroscopic aggregations of emulsifier molecules. Critical micelle concentration is slightly different for each emulsifier, usable concentrations ranging from about 1.0×10^{-4} to about 3.0 moles/liter. Additional detail concerning the preparation of water-in-oil-in-water emulsions, i.e., multiple emulsions, may be found in various literature references, e.g., *Surfactant Systems: Their Chemistry, Pharmacy, & Biology*, (D. Attwood and A. T. Florence, Chapman & Hall Limited, New York, N.Y., 1983). The final process step of this method of the invention involves the application of heat or radiation to initiate polymerization of the monomers. Useful initiators are those which are normally suitable for free radical polymerization of acrylate monomers and which are oil-soluble and of very low solubility in water. However, when the nitrogen-containing polar monomer is N-vinyl pyrrolidone, the use of benzoyl peroxide as the initiator is recommended. Examples of such initiators include thermally-activated initiators such as azo compounds, hydroperoxides, peroxides, and the like, and photoinitiators such as benzophenone, benzoin ethyl ether, and 2,2-dimethoxy-2-phenyl acetophenone. Use of a water-soluble polymerization initiator causes formation of substantial amounts of latex. The extremely small particle size of latex particles renders any significant formation of latex undesirable. The initiator is generally used in an amount ranging from about 0.01 percent up to about 10 percent by weight of the total polymerizable composition, preferably up to about 5 percent.

Aqueous suspensions of hollow acid-free microspheres may also be prepared by a "one-step" emulsification process comprising aqueous suspension polymerization of at least one alkyl acrylate or alkyl methacrylate ester monomer and at least one nitrogen-containing polar monomer in the presence of at least one emulsifier capable of producing a water-in-oil emulsion inside the droplets which is substantially stable during emulsification and polymerization. As in the two-step emulsification process, the emulsifier is utilized in concentrations greater than its critical micelle concentration. In general, high HLB emulsifiers are required, i.e., emulsifiers having an HLB value of at least about 25, will produce stable cavity-containing droplets during the polymerization, and are suitable for use in this one-step process. Examples of such emulsifiers include alkylarylether sulfates such as sodium alkylarylether sulfate, e.g., Triton™ W/30, available from Rohm and Haas, alkylaryl polyether sulfates such as alkylaryl poly(ethylene

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oxide) sulfates, preferably those having up to about 4 ethyleneoxy repeat units, and alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, and sodium hexadecyl sulfate, alkyl ether sulfates such as ammonium lauryl ether sulfate, and alkylpolyether sulfates such as alkyl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy units. Alkyl sulfates, alkyl ether sulfates, and alkylarylether sulfates are preferred as they provide a maximum number of voids per microsphere for a minimum amount of surfactant. Polymeric stabilizers may also be present but are not necessary.

The composition may also contain a crosslinking agent such as a multifunctional (meth)acrylate, e.g., butanediol diacrylate or hexanediol diacrylate, or other multifunctional crosslinker such as divinylbenzene. When used, crosslinker(s) is (are) added at a level of up to about 0.5 mole percent, preferably up to about 0.1 mole percent, of the total polymerizable composition.

The hollow acid-free microspheres of the invention are normally tacky, elastomeric, insoluble but swellable in organic solvents, and small, typically having diameters of at least about 1 micrometer, preferably in the range of about 1 to about 250 micrometers. The majority of the hollow acid-free microspheres prepared by the methods of this invention contain multiple voids, a majority of the voids having a diameter which is less than about 10% of the diameter of the microsphere, the total of all the void diameters being at least about about 10% of the diameter of the microsphere, preferably at least about 20%, more preferably, at least about 30%.

Following polymerization, an aqueous suspension of the hollow microspheres is obtained which is stable to agglomeration or coagulation under room temperature conditions. The suspension may have non-volatile solids contents of from about 10 to about 50 percent by weight. Upon prolonged standing, the suspension separates into two phases, one phase being aqueous and substantially free of polymer, the other phase being an aqueous suspension of microspheres having multiple cavities which, upon drying, become voids. Both phases may contain a minor portion of small latex particles. Decantation of the microsphere-rich phase provides an aqueous suspension having a non-volatile solids content on the order of about 40-50 percent which, if shaken with water, will readily redisperse. If desired, the aqueous suspension of hollow microspheres may be utilized immediately following polymerization to provide inherently tacky pressure-sensitive adhesive coatings. The suspension may be coated on suitable flexible or inflexible backing materials by conventional coating techniques such as knife coating or Meyer bar coating or use of an extrusion die.

Alternatively, the aqueous suspension may be coagulated with polar organic solvents such as methanol, with ionic emulsifiers having a charge opposite to that of the emulsifier used in the polymerization process, or with saturated salt solutions, or the like, followed by washing and drying. The dried hollow microspheres, with sufficient agitation, will readily disperse in common organic liquids such as ethyl acetate, tetrahydrofuran, heptane, 2-butanone, benzene, cyclohexane, and esters, although it is not possible to resuspend them in water. Solvent dispersions of the hollow microspheres may also be coated on suitable backing materials by conventional coating techniques, as described above for aqueous suspensions.

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Suitable backing materials for the aqueous or solvent based coatings include paper, plastic films, cellulose acetate, ethyl cellulose, woven or nonwoven fabric formed of synthetic or natural materials, metal, metalized polymeric film, ceramic sheet material, and the like. Primers or binders may be used, but they are not required.

Suspensions or dispersions of the hollow acid-free microspheres in a liquid medium, e.g., water or an organic liquid as described above, may be sprayed by conventional techniques without cobwebbing or may be incorporated in aerosol containers with suitable propellants such as alkanes, alkenes, or chlorofluorocarbons, e.g., Freons™. The hollow acid-free microspheres of the invention provide a repositionable pressure-sensitive adhesive, i.e., a pressure-sensitive adhesive having a degree of adhesion which permits separation, repositioning, and rebonding.

Useful aerosol formulae have a solids content of from about 5% to about 20%, preferably from about 10% to about 16%.

The pressure-sensitive adhesive properties of the acid-free hollow microspheres may be altered by addition of tackifying resin and/or plasticizer. Preferred tackifiers for use herein include hydrogenated rosin esters commercially available from companies such as Hercules Inc., under such trade names as Foral™, and Pentalyn™. Individual tackifiers include Foral™ 65, Foral™ 85, and Foral™ 105. Other useful tackifiers include those based on t-butyl styrene. Useful plasticizers include dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate, and the like.

It is also within the scope of this invention to include various other components, such as pigments, fillers, stabilizers, or various polymeric additives.

These and other aspects of the invention are illustrated by the following examples which should not be viewed as limiting in scope.

TEST METHODS

Peel Adhesion

Peel adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in grams per centimeter (cm) width of coated sheet. The procedure followed is:

A strip 1.27 cm in width of the coated sheet is applied to the horizontal surface of a clean glass test plate with at least 12.7 lineal cm in firm contact. A 2 kg hard rubber roller is used to apply the strip. The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 180°. The free end is attached to the adhesion tester scale. The glass test plate is clamped in the jaws of a tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute. The scale reading in grams is recorded as the tape is peeled from the glass surface. The data is reported as the average of the range of numbers observed during the test.

Shear Strength

The shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the amount of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pres-

sure. It is measured in minutes required to pull a standard area of adhesive coated sheet material from a stainless steel test panel under stress of a constant, standard load.

The tests were conducted on strips of coated sheet material applied to a stainless steel panel such that a 1.27 cm by 1.27 cm portion of each strip was in firm contact with the panel with one end portion of the tape being free. The panel with the coated strip attached was held in a rack such that the panel formed an angle of 178° with the extended tape free end which was tensioned by application of a force of 200 grams applied as a hanging weight from the free end of the coated strip. The 2° less than 180° is used to negate any peel forces, thus insuring that only the shear forces are measured, in an attempt to more accurately determine the holding power of the tape being tested. The time elapsed for each coated film to separate from the test panel was recorded as the shear strength.

EXAMPLE 1

In a one-liter reactor equipped with mechanical stirrer, condenser, and inlet-outlet lines for vacuum and argon, 450 grams of deionized water, 135 grams of isooctyl acrylate, 15 grams of N-vinyl-2-pyrrolidone, 0.04 gram of 1,4-butanediol diacrylate and 0.5 gram of benzoyl peroxide were charged. Vacuum was applied to evacuate the reactor atmosphere, and the reactor was then purged with argon. The agitation was set to 400 RPM and when the initiator had dissolved 1.5 grams of ammonium lauryl sulfate (Standapol TM A, Henkel AG) were added. The temperature of the reactor was raised to 60° C. and maintained for 22 hours. An argon purge was maintained during the polymerization. After the 22-hour period, the suspension was allowed to cool to room temperature. The reactor was then emptied and the suspension filtered. Optical microscopy showed hollow microspheres from about 10 to 85 micrometers in diameter suspended in water. The majority of the microspheres contained multiple inclusions at least about 2 micrometers in diameter.

EXAMPLES 2-7

These examples illustrate the use of N-vinyl-2-pyrrolidone in different amounts and with different acrylates to prepare hollow, tacky elastomeric microspheres using the type of equipment and polymerization technique outlined in Example 1. Details of the compositions are listed in Table I. For these examples the initiator was benzoyl peroxide (0.5 grams) and the surfactant was ammonium lauryl sulfate (1.5 grams). All polymerizations produced aqueous suspensions of hollow microspheres. The microspheres contained multiple inclusions at least about 2 microns in diameter.

TABLE I

| Example | Monomers |
|---------|---|
| 2 | 135 g isooctyl acrylate 15 g N-vinyl-2-pyrrolidone 0.08 g 1,4-butanediol diacrylate |
| 3 | 127.5 g isooctyl acrylate 22.5 g N-vinyl-2-pyrrolidone 0.04 g 1,4-butanediol diacrylate |
| 4 | 112.5 g isooctyl acrylate 37.5 g N-vinyl-2-pyrrolidone 0.04 g 1,4-butanediol diacrylate |
| 5 | 105 g isooctyl acrylate 45 g N-vinyl-2-pyrrolidone 0.04 g 1,4-butanediol diacrylate |
| 6 | 135 g 2-ethylhexyl acrylate |

TABLE I-continued

| Example | Monomers |
|---------|---|
| 7 | 15 g N-vinyl-2-pyrrolidone 67.5 g isooctyl acrylate 75 g n-butyl acrylate 7.5 g N-vinyl-2-pyrrolidone 0.08 g trimethylolpropane trimethacrylate |

EXAMPLES 8-13

These examples illustrate the use of different N-containing polar monomers to prepare hollow tacky microspheres. The equipment and technique used to prepare the microsphere suspensions were similar to those described in Example 1. In these examples the initiator used was benzoyl peroxide (0.5 gram) except for Example 9 where 0.5 g of 2,2'-azobis(2,4-dimethylpentane nitrile), available from DuPont as Vazo TM -52 initiator was used. The surfactant in all examples was ammonium lauryl sulfate (1.5 grams) except for Example 12 where 1.0 g of sodium cetyl sulfate was used. Monomer compositions are shown in Table II.

TABLE II

| Example | Monomers |
|---------|---|
| 8 | 135 g isooctyl acrylate 15 g vinyl caprolactam 0.04 g 1,4-butanediol diacrylate |
| 9 | 135 g isooctyl acrylate 15 g 2-vinyl-4,4-dimethyl-2-oxazolin-5-one 0.08 g divinyl benzene |
| 10 | 144 g isooctyl acrylate 6 g dimethylaminoethyl methacrylate 0.04 g 1,6-hexanediol diacrylate |
| 11 | 141 isooctyl acrylate 9 g octyl acrylamide 0.02 g tetraethylene glycol dimethacrylate |
| 12 | 120 g 2-ethylhexyl acrylate 15 g n-butyl acrylate 7.5 g N-vinyl-2-pyrrolidone 7.5 g 2-vinyl-4,4-dimethyl-2-oxazolin-5-one 0.02 g trimethylolpropane trimethacrylate |
| 13 | 127.5 g isodecyl acrylate 22.5 N-vinyl caprolactam 0.08 g divinyl benzene |

EXAMPLE 14

The microspheres of Example 1 were coagulated and dispersed in isopropanol at 12 wt% solids. The solvent dispersion was coated on 100# weight white paper and dried. The microsphere pressure sensitive adhesive dry coating weight was 18 g/m². The microsphere coated paper and an acid-sensitive substrate were repeatedly attached to each other and separated. A 90° peel adhesion of 67.3 g/cm was recorded. Adhesion and removability were good. No transfer of microspheres or damage to the acid sensitive substrate was observed.

EXAMPLES 15 TO 21

Microspheres prepared in the examples shown in Table III were coagulated and dispersed in isopropanol or isopropanol/heptane mixtures and coated on a 37-micron thick poly(ethylene terephthalate) film. The coatings were dried in an oven at 65° C. for 10 minutes and left in a constant humidity (50% relative humidity) and temperature (22.2° C.) room overnight. The coated samples were tested for peel adhesion and shear strength. Results are shown in Table III. Examples 16, 17, 19, and 20 show excellent shear performance. Examples 16 and 17, which have high levels of the N-contain-

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ing polar monomer show exceptional shear performance for a repositionable adhesive.

TABLE III

| Example | Microsphere Example | Coating Weight (g/m ²) | Peel Adhesion (g/cm) | Shear Strength (minutes) |
|---------|---------------------|------------------------------------|----------------------|--------------------------|
| 15 | 1 | 5 | 124.3 | 6.0 |
| 16 | 3 | 5 | 191.3 | >3,000.0 |
| 17 | 5 | 5 | 105.6 | >3,000.0 |
| 18 | 7 | 9 | 69.2 | 11.0 |
| 19 | 8 | 7 | 259.6 | 32.0 |
| 20 | 9 | 5 | 205.4 | 493.5 |
| 21 | 10 | 7 | 152.5 | 7.5 |

What is claimed is:

1. Hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres having an average diameter of at least about 1 micrometer to about 250 micrometers wherein a majority of said microspheres contain multiple interior voids, a majority of said voids having a diameter of less than about 10% of the diameter of the microsphere, the total of the void diameters being at least about 10% of the diameter of said hollow microsphere.

2. Hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres having an average diameter of at least about 1 micrometer wherein a majority of said microspheres contain multiple interior voids, a majority of said voids having a diameter of less than about 10% of the diameter of the microsphere, the total of the void diameters being at least about 20% of the diameter of said hollow microsphere.

3. Hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres having an average diameter of at least about 1 micrometer wherein a majority of said microspheres contain multiple interior voids, a majority of said voids having a diameter of less than about 10% of the diameter of the microsphere, the total of the void diameters being at least about 30% of the diameter of said hollow microsphere.

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4. Hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres according to claim 1 comprising:

5 (a) at least about 70 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester, and
(b) correspondingly, up to about 30 parts by weight of at least one nitrogen-containing polar monomer.

5. Hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric, nitrogen-containing, acid-free pressure-sensitive adhesive microspheres according to claim 1 comprising:

(a) at least about 85 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester, and
15 (b) correspondingly, up to about 15 parts by weight of at least one nitrogen-containing polar monomer.

6. The hollow acid-free microspheres of claim 4 wherein the alkyl acrylate is selected from the group consisting of isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate and butyl acrylate.

7. The hollow acid-free microspheres of claim 6 wherein the nitrogen-containing polar monomer is selected from the group consisting of N-vinyl-2-pyrrolidone, N-vinyl caprolactam, 2-vinyl-4,4-dimethyl-2-oxazolin-5-one, dimethylaminoethyl methacrylate, acrylamide, t-butyl acrylamide and N-octyl acrylamide.

8. A particulate pressure-sensitive adhesive consisting essentially of the hollow acid-free microspheres of claim 1.

9. A particulate pressure-sensitive adhesive consisting essentially of the hollow acid-free microspheres of claim 4.

10. A particulate pressure-sensitive adhesive consisting essentially of the hollow microspheres of claim 7.

11. A repositionable spray pressure-sensitive adhesive comprising the hollow microspheres of claim 1 and a liquid medium therefor.

12. A repositionable spray pressure-sensitive adhesive according to claim 11 further comprising a propellant selected from the group consisting of alkanes, alkenes, and chlorofluorocarbons.

13. A sheet material having coated on at least a portion thereof the pressure-sensitive adhesive of claim 8.

14. An aqueous suspension comprising the hollow microspheres of claim 1.

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United States Patent [19]

Delgado et al.

[11] Patent Number: 4,994,322

[45] Date of Patent: Feb. 19, 1991

[54] PRESSURE-SENSITIVE ADHESIVE
COMPRISING HOLLOW TACKY
MICROSPHERES AND
MACROMONOMER-CONTAINING BINDER
COPOLYMER

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525/218; 525/221; 525/228

[58] Field of Search 428/343, 355, 402;
521/54, 56, 60, 63, 64, 134; 523/223; 524/801;
525/205

ABSTRACT

A repositionable pressure-sensitive adhesive comprising
from about 70% to about 99% hollow, polymeric, acry-
late, inherently tacky, infusible, solvent-insoluble, sol-
vent-dispersible, elastomeric microspheres comprising
at least one alkyl acrylate or alkyl methacrylate ester, a
majority of the microspheres having one or more inter-
ior voids having a diameter of at least about 10% of the
diameter of the microsphere, and correspondingly,
from about 30% to about 1% of a binder copolymer
comprising an elastomeric polymeric backbone having
pendant therefrom high Tg polymeric moieties.

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16 Claims, No Drawings

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PRESSURE-SENSITIVE ADHESIVE COMPRISING HOLLOW TACKY MICROSPHERES AND MACROMONOMER-CONTAINING BINDER COPOLYMER

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a composition containing a dispersion of hollow polymeric, acrylate, infusible, inherently tacky, elastomeric, solventdispersible, solvent-insoluble microspheres and a soluble macromonomer-containing copolymer, and to their use as sprayable repositionable pressure-sensitive adhesives.

2. Description of the Related Art

Solid, inherently tacky, elastomeric microspheres are known in the art to be useful in repositionable pressure-sensitive adhesive applications. As used herein, the term "repositionable" refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability. Microsphere-based adhesives are thought to perform well in such applications at least in part due to their "self-cleaning" nature, wherein substrate contaminants tend to be pushed aside and trapped between the microspheres as the adhesive is applied. Upon removal, the adhesive then still presents a relatively uncontaminated surface for reapplication to the substrate.

Such spheres and their use in aerosol adhesive systems having repositionable properties are disclosed in U.S. Pat. No. 3,691,140 (Silver). These microspheres are prepared by aqueous suspension polymerization of alkyl acrylate monomers and ionic comonomers, e.g., sodium methacrylate, in the presence of an emulsifier, preferably an anionic emulsifier. The use of a water-soluble, substantially oil-insoluble ionic comonomer is critical to preventing coagulation or agglomeration of the microspheres.

U.S. Pat. No. 4,166,152, (Baker et al.) describes solid, inherently tacky (meth)acrylate microspheres which are prepared from non-ionic alkyl acrylate or methacrylate monomer(s) in the presence of both an emulsifier and an ionic suspension stabilizer having an interfacial tension sufficient to prevent microsphere agglomeration. Such microspheres are also disclosed in U.S. Pat. Nos. 4,495,318 and 4,598,112 (Howard), where the preparative methods involve the use of a nonionic emulsifier or a cationic emulsifier. All three patents disclose utility as a "reusable adhesive".

U.S. Pat. No. 4,786,696, (Bohnel) describes a suspension polymerization process for preparing solid, inherently tacky (meth)acrylate microspheres which does not require the use of either an ionic comonomer or an ionic suspension stabilizer in order to prevent agglomeration. Rather, the process requires agitation of the vessel charge prior to the initiation of the reaction sufficient to create a suspension of monomer droplets having an average monomer droplet size of between about 5 and about 70 micrometers. In addition to (meth)acrylate monomer, a minor portion of a non-ionic, vinylic comonomer such as, e.g., acrylic acid may be included to modify the "tacky nature" of the microspheres.

The primary problem associated with these types of adhesives have been microsphere loss, i.e., microsphere transfer to the substrate. The problem is exacerbated when the microspheres are used in aerosol form. This

has typically been addressed by the use of a binder or primer for the microspheres.

U.S. Pat. No. 3,857,731, (Merrill et al.) and EPA 0209337, Thomson et al. both address microsphere transfer problems. The former discloses sheets coated with tacky elastomeric copolymer microspheres and a binder material which provides sockets in which the microspheres are held by predominately mechanical forces. Additional chemical forces are not required; in fact, it is further stated at column 1, at line 62 that the binder "need not have a high degree of adhesion for the microspheres, and in fact, binders having an extremely low adhesion for the microspheres provide an excellent microsphere retaining surface". A wide range of useful binders are disclosed including hard resins such as an epoxy or nitrocellulose composition, soft resins such as an acrylate or vinyl ether, urethanes, fluorochemicals, silicones and microcrystalline waxes. Preferably, the binder is used at a level of 0.20 to 0.60 parts of binder to 1 part microspheres. Adhesives are disclosed to have a maximum adhesion of 25.9 g/cm.

EPA 0209337, (Thomson et al.) discloses microsphere adhesives which may contain an adhesion promoting monomer, such as a vinyl pyridine, having functionality which remains unreacted during polymerization, and is therefore available for subsequent binding of the microspheres through electrostatic interaction or chemical bonding to a substrate, which may be primed. It is disclosed that a binder may be blended with the microspheres.

DE 3,544,882 A1, (Nichiban), describes crosslinked microspheres composed of (meth)acrylate ester and vinyl type monomer, e.g., acrylic acid, having a reactive functional group through which crosslinking is achieved. When tacky, the spheres are said to be useful in spray or coated sheet form as "removable adhesive". The microspheres may contain other monomers to prevent partial transfer of the adhesive when the backing is pulled away from the substrate. Monomers disclosed as useful include vinyl acetate, styrene, and acrylonitrile. The additional monomers may be present in amounts up to 50 percent of the (meth)acrylate ester monomer.

U.S. Pat. No. 4,735,837, (Miyasaka et al.) discloses a detachable adhesive sheet having an adhesive layer containing "elastic micro-balls" with the ratio of adhesive to micro-balls being from about 1:10 to about 10:1. The density of the micro-balls for an optimal balance of adhesive and removability is disclosed to be from 1,000 to 150,000 pieces per square centimeter. The micro-balls may or may not be tacky. They can be derived from, e.g., (meth)acrylate monomer and an α -olefinic carboxylic acid monomer via suspension polymerization in an aqueous medium. However, no details as to the nature of the surfactants utilized, etc., are disclosed. The micro-balls and an adhesive are dispersed in solvent, mixed, and coated, with the ratio of adhesive to micro-balls being from about 1:10 to about 10:1. This ratio is disclosed to be critical in order that all micro-balls in the final product, including those protruding from the surface, are completely covered with the adhesive.

U.S. Pat. No. 4,810,763 (Mallya et al.) discloses inherently tacky infusible pressure-sensitive adhesive microspheres. It is stated that the microspheres must have a adhesion of 57-92 N/m (59-95 g/cm) to stainless steel at a peel rate of 300 inches/minute, after 20 minutes dwell, when adhered with a 4.5 pound roller, to provide good performance.

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U.S. Pat. No. 4,656,218, (Kinoshita) discloses a releasable sheet coated with a microsphere adhesive prepared by suspension polymerization followed by emulsion polymerization wherein a latex binder is formed in situ from alpha-olefin carboxylic acids such as acrylic acid. The latex is disclosed to consist of microparticles having average diameter of from 1-4 microns. The binder is stated to have no effect on the properties of the adhesive, and to be effective in improving the anchorage of the microspheres to the substrate. Tackifiers are disclosed as preferred optional ingredients.

U.S. Pat. No. 4,049,483, (Loder et al.) blends pressure-sensitive adhesive microspheres with hot-melt adhesives to impart temporary pressure-sensitive bonding ability to a hot-melt film. A typical composition, containing about 27% tackified microspheres had adhesion of about 14 g/inch. Other compositions exhibited adhesion of from 14 g/inch up to a high of about 24 g/inch (5.5 -9.4g/cm).

In an aerosol adhesive, the sprayability of the adhesive is critical. Several patents disclose nonparticulate adhesives having good sprayability. U.S. Pat. No. 3,578,622, (Brown et al.), discloses an acrylate aerosol spray adhesive which is non-cobwebbing, and does not form rubbery strings. The aerosol composition contains at least 2% of a pressure-sensitive crosslinked, elastomeric, acrylate polymer having an insolubility index of from about 0.5 and 0.97, and a carrier liquid. Acrylic acid esters are disclosed as preferred acrylate polymers. The use of a tackifier is also disclosed.

Another aerosol adhesive is disclosed in U.S. Pat. No. 3,400,095, (Kremer et al.) wherein the aerosol comprises a crosslinked, insoluble, dispersed rubber polymer containing a tackifier resin, from 0.3 to 3% of a soluble elastomer, and an organic liquid. The use of the soluble elastomer is disclosed to control the sprayability, providing a one inch spray width without excess misting or cobwebbing.

U.S. Pat. No. 4,554,324, (Husman et al.) discloses a pressure-sensitive adhesive comprising a polymer having an inherent viscosity greater than 0.2 and having in its backbone at least a major portion by weight of polymerized monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, and having attached to the backbone polymeric moieties having a weight average molecular weight of above 2000 and a T_g of 20° C or higher.

It has now been discovered that a particulate, i.e., microsphere adhesive with excellent sprayability, improved peel adhesion and low adhesive transfer can be made by combining hollow, polymeric, acrylate, inherently tacky elastomeric microspheres with a binder copolymer containing a macromolecular monomer.

SUMMARY OF THE INVENTION

This invention provides pressure-sensitive adhesives comprising hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres, and at least about 1% of a macromolecular-monomer containing (macromonomer-containing) elastomeric binder copolymer.

Preferred hollow microspheres for use in the pressure-sensitive adhesives contain one or more interior voids having diameters at least about 10% of the diameter of the microsphere.

The invention further provides organic dispersions of the microspheres and binder copolymers, spray deposi-

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tionable pressure-sensitive adhesive compositions, and sheet materials coated therewith.

More specifically, the pressure-sensitive adhesive comprises from about 70% to about 99% of

(a) hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres comprising at least one alkyl acrylate or alkyl methacrylate ester, a majority of the microspheres having one or more interior voids having a diameter of at least about 10% of the diameter of the microsphere, and

(b) correspondingly, from about 30% to about 1% of a binder copolymer comprising an elastomeric polymeric backbone having pendant therefrom polymeric moieties, such backbone containing repeating A and C monomers, and from about 1% to about 20% B monomers, wherein

A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms, with the average number of carbon atoms being about 4-12, said A monomer comprising from about 50% to about 98% of said monomers;

B is a polar monomer copolymerizable with said monomeric acrylic acid ester;

C is a monomer having the general formula $X-(Y)_n-Z$, wherein X is a vinyl group copolymerizable with said A and B monomers;

Y is a divalent linking group, where n is zero or 1, and

Z is a monovalent polymeric moiety having a T_g greater than 20° C, and a molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions, C comprising from about 1% to about 30% of said monomers,

wherein said binder copolymer has a shear storage modulus of at least about 1×10^8 Pascals at 22° C

Preferably, the pressure-sensitive adhesive comprises from about 70% to about 99% of

(a) hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres comprising

(i) at least about 85 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester; and

(ii) up to about 15 parts by weight of at least one polar monomer, a majority of the microspheres having one or more interior voids having a diameter of at least about 30% of the diameter of the microsphere, and

(b) correspondingly, from about 30% to about 1% of a binder copolymer comprising an elastomeric polymeric backbone having pendant therefrom polymeric moieties, such backbone containing repeating A and C monomers and from about 1% to about 20% B monomers, wherein

A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms, with the average number of carbon atoms being about 4-12, said A monomer comprising from about 50% to about 98% of said monomers;

B is a polar monomer copolymerizable with said acrylic acid ester;

C is a monomer having the general formula $X-(Y)_n-Z$, wherein X is a vinyl group copolymerizable with said A and B monomers,

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Y is a divalent linking group, where n is zero or 1, and

Z is a monovalent polymeric moiety having a T_g greater than 20°C , and a molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions, C comprising from about 1% to about 30% of said monomers,

wherein said binder copolymer has a shear storage modulus of at least about 1.0×10^5 Pascals at 22°C .

The following terms have these meanings as used herein:

1. The term "droplet" means the liquid stage of the microspheres prior to the completion of polymerization.

2. The term "cavity" means a space within the walls of a droplet or microsphere when still in the suspension or dispersion medium prior to drying, and thus containing whatever medium was used.

3. The term "void" means an empty space completely within the walls of a polymerized microsphere.

4. The term "hollow" means containing at least one void or cavity.

5. A "macromonomer" means a macromolecular monomer as disclosed in U.S. Pat. No. 3,786,111.

6. The terms "macromonomer-containing binder copolymer", "binder copolymer", "elastomeric binder copolymer", and the like are used interchangeably to refer to macromolecular monomer-containing elastomeric binder copolymers.

All weights, parts, and ratios herein are by weight unless specifically stated otherwise.

DETAILED DESCRIPTION OF THE INVENTION

The pressure-sensitive adhesives of the invention comprise from about 70% to about 99% hollow microspheres, and correspondingly from about 30% to about 1% of a solvent-soluble, macromonomer-containing binder copolymer.

The hollow microspheres comprise at least one alkyl acrylate or alkyl methacrylate ester and one or more polar monomers. Preferably, at least one polar monomer is included in the composition, but hollow microspheres may also be prepared using acrylate or methacrylate monomer(s) alone or in combination only with other vinyl monomers, e.g., vinyl acetate. However, when methacrylate monomer alone is utilized, a cross-linking agent, *infra*, must be included. For most polar monomers, incorporation of from about 1 part to about 10 parts by weight is preferred, as this ratio provides hollow microspheres with balanced pressure-sensitive adhesive properties.

Alkyl acrylate or methacrylate monomers useful in preparing the hollow microspheres for pressure-sensitive adhesives of this invention are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to about 14 carbon atoms. Such acrylates are oleophilic, water emulsifiable, have restricted water solubility, and as homopolymers, generally have glass transition temperatures below about -20°C . Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, and the like, singly or in mixtures.

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Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate, and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have glass transition temperatures higher than about -20°C , e.g., tert-butyl acrylate, isobornyl acrylate, butyl methacrylate, vinyl acetate, N-vinyl pyrrolidone, acrylamide, and the like, may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is below about -20°C .

Polar monomers suitable for copolymerization with the acrylate or methacrylate monomers are those polar monomers which are both somewhat oil-soluble and watersoluble.

Representative examples of suitable polar monomers include weakly to moderately ionized polar monomers such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, sulfoethyl methacrylate, and ionic monomers such as sodium methacrylate, ammonium acrylate, sodium acrylate, trimethylamine p-vinyl benzimide, 4,4,9-trimethyl-4-azonia-7-oxo-8-oxa-dec-9-ene-1-sulphonate, N,N-dimethyl-N-(β -methacryloxyethyl) ammonium propionate betaine, trimethylamine methacrylimide, 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide, and the like. Preferred polar monomers are monoolefinic, mono- and dicarboxylic acids, salts thereof, and mixtures thereof.

Preferred microspheres of the invention comprise at least about 85 parts of the alkyl acrylate monomer(s), and correspondingly up to about 15 parts of the polar monomer(s).

Aqueous suspensions of the hollow microspheres may be prepared by a "two-step" emulsification process which first involves forming a water-in-oil emulsion of an aqueous solution of polar monomers in oil phase monomer, i.e., at least one acrylate or methacrylate ester, using an emulsifier having a low hydrophilic-lipophilic balance (HLB) value. Where it is desirable not to include a polar monomer, water may be mixed directly with the oil phase monomer, i.e., acrylate or methacrylate ester, and emulsifier to form the water-in-oil emulsion. Suitable emulsifiers are those having an HLB value below about 7, preferably in the range of about 2 to about 7. Examples of such emulsifiers include sorbitan mono-oleate, sorbitan trioleate, and ethoxylated oleyl alcohol such as Brij TM 93, available from Atlas Chemical Industries, Inc. Thus, in this first step, oil phase monomer(s), emulsifier, a free radical initiator, and, optionally, a crosslinking monomer or monomers as defined below are combined, and an aqueous solution of all or a portion of the polar monomer(s) is agitated and poured into the oil phase mixture to form a water-in-oil emulsion. A thickening agent, e.g., methyl cellulose may also be included in the aqueous phase of the water-in-oil emulsion. In the second step, a water-in-oil-in-water emulsion is formed by dispersing the water-in-oil emulsion of the first step into an aqueous phase containing an emulsifier having an HLB value above about 6. The aqueous phase may also contain any portion of the polar monomer(s) which was not added in step one. Examples of such emulsifiers include ethoxylated sorbitan mono-oleate, ethoxylated lauryl alcohol, and alkyl sulfates. In both steps, when an emulsifier is utilized, its concentration should be greater than its critical micelle concentration, which is herein defined as the minimum

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concentration of emulsifier necessary for the formation of micelles, i.e., submicroscopic aggregations of emulsifier molecules. Critical micelle concentration is slightly different for each emulsifier, usable concentrations ranging from about 1.0×10^{-4} to about 3.0 moles/liter. Additional detail concerning the preparation of water-in-oil-in-water emulsions, i.e., multiple emulsions, may be found in various literature references, e.g., *Surfactant Systems: Their Chemistry, Pharmacy, & Biology*, (D. Attwood and A. T. Florence, Chapman & Hall Limited, New York, New York, 1983). The final process step of this method of the invention involves the application of heat or radiation to initiate polymerization of the monomers. Suitable initiators are those which are normally suitable for free radical polymerization of acrylate monomers and which are oil-soluble and of very low solubility in water. Examples of such initiators include thermally-activated initiators such as azo compounds, hydroperoxides, peroxides, and the like, and photoinitiators such as benzophenone, benzoin ethyl ether, and 2,2-dimethoxy-2-phenyl acetophenone. Use of a water-soluble polymerization initiator causes formation of substantial amounts of latex. The extremely small particle size of latex particles renders any significant formation of latex undesirable. The initiator is generally used in an amount ranging from about 0.01 percent up to about 10 percent by weight of the total polymerizable composition, preferably up to about 5 percent.

Aqueous suspensions of hollow microspheres which contain moderately ionized polar monomer(s) may also be prepared by a "one-step" emulsification process comprising aqueous suspension polymerization of at least one alkyl acrylate or alkyl methacrylate ester monomer and at least one moderately ionized polar monomer in the presence of at least one emulsifier capable of producing a water-in-oil emulsion inside the droplets which is substantially stable during emulsification and polymerization. As in the two-step emulsification process, the emulsifier is utilized in concentrations greater than its critical micelle concentration. In general, high HLB emulsifiers are required, i.e., emulsifiers having an HLB value of at least about 25, will produce stable cavity-containing droplets during the polymerization, and are suitable for use in this one-step process. Examples of such emulsifiers include alkylarylether sulfates such as sodium alkylarylether sulfate, e.g., Triton TM W/30, available from Rohm and Haas, alkylaryl-polyether sulfates such as alkylaryl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy repeat units, and alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, and sodium hexadecyl sulfate, alkyl ether sulfates such as ammonium lauryl ether sulfate, and alkyl-polyether sulfates such as alkyl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy units. Alkyl sulfates, alkyl ether sulfates, and alkylarylether sulfates are preferred as they provide a maximum void volume per microsphere for a minimum amount of surfactant. Polymeric stabilizers may also be present but are not necessary.

The composition may also contain a crosslinking agent such as a multifunctional (meth)acrylate, e.g., butanediol diacrylate or hexanediol diacrylate, or other multifunctional crosslinker such as divinylbenzene.

The hollow microspheres are normally tacky, elastomeric, insoluble but swellable in organic solvents, and small, typically having diameters of at least 1 micrometer, preferably in the range of about 1 to about 250

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micrometers. The voids typically range in size up to about 100 micrometers or larger. The majority of the hollow microspheres contain at least one void with a void diameter which is at least about 10% of the diameter of the microsphere, preferably at least about 20%, more preferably, at least about 30%.

Following polymerization, an aqueous suspension of the hollow microspheres is obtained which is stable to agglomeration or coagulation under room temperature conditions. The suspension may have non-volatile solids contents of from about 10 to about 50 percent by weight. Upon prolonged standing, the suspension separates into two phases, one phase being aqueous and substantially free of polymer, the other phase being an aqueous suspension of microspheres having at least one cavity, which, upon drying, becomes a void. Both phases may contain a minor portion of small latex particles. Decantation of the microsphere-rich phase provides an aqueous suspension having a non-volatile solids content on the order of about 40-50 percent which, if shaken with water, will readily redisperse.

The aqueous suspension may be coagulated with polar organic solvents such as methanol, with ionic emulsifiers having a charge opposite to that of the emulsifier used in the polymerization process, or with saturated salt solutions, or the like, followed by washing and drying. The dried hollow microspheres, with sufficient agitation, will readily disperse in common organic liquids such as ethyl acetate, tetrahydrofuran, heptane, 2-butanone, benzene, cyclohexane, and esters, although it is not possible to resuspend them in water.

Binder copolymers useful in adhesives of the invention are copolymers having an inherent viscosity of at least about 0.4 dl/g. For aerosol applications, the preferred range is from about 0.4 to about 1.2 dl/g. The copolymers contain repeating units of A and C monomers, and B monomers. A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alkyl alcohol having an average number of carbon atoms from about 4-12. B is a polar monomer copolymerizable with the monomeric acrylic acid ester. Preferred B monomers are acrylic acid, methacrylic acid, acrylamide, methacrylamide, and N-vinyl pyrrolidone. The B monomer(s) are present in amounts from about 1 part to about 20 parts. The C monomer has the general formula $X(Y)_nZ$ wherein X is a vinyl group copolymerizable with the A and B monomers, Y is a divalent linking group wherein n can be either zero or one, and Z is a monovalent polymeric moiety having a T_g greater than 20° C and a weight average molecular weight in the range of about 2,000 to 30,000 and being essentially unreactive under copolymerization conditions. The vinyl group of the C monomer and the A and B monomers are copolymerized to form an elastomeric backbone having the polymeric moieties pendant therefrom. The weight of the C monomer is within the range of about 1 to about 30% of the weight of all monomers. The total weight of the B and C monomers is from about 2% to about 50% of the weight of all monomers in the copolymer.

Monomer A, as previously mentioned, is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms with the average number of carbon atoms being about 4-12. Examples of such monomers include the esters of acrylic acid or methacrylic acid with non-tertiary alkyl alcohols such as 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-

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pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, 1-dodecanol, isooctyl alcohol, isononyl alcohol, 2-ethyl-hexyl alcohol, and the like. Such monomeric acrylic or methacrylic esters are known in the art and many are commercially available.

As mentioned above, the B monomer is copolymerizable with the monomeric acrylic acid ester. Preferred B monomers are acrylic acid, methacrylic acid, itaconic acid, N-vinyl pyrrolidone, acrylamide, substituted acrylamides, e.g. n-octyl acrylamide, methacrylamide, acrylonitrile and methacrylonitrile. The B monomer comprises from about 1% up to about 20% of the total weight of all monomers. The preferred binder copolymer according to the present invention will contain from 1 to 15% by weight of B monomer.

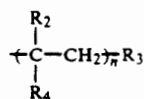
The C monomer is a polymeric material having a copolymerizable vinyl moiety with which the A monomer and the B monomer will copolymerize under the polymerization conditions. The C monomer is represented by the general formula $X(Y)_nZ$ as described infra.

The preferred C monomer may be further defined as having an X group which has the general formula

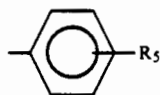


wherein R is a hydrogen atom or a COOH group and R' is a hydrogen atom or methyl group. The double bond between the carbon atoms provides a copolymerizable moiety capable of copolymerizing with the A and B monomers.

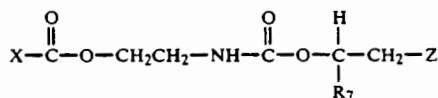
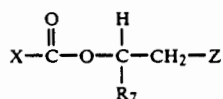
The preferred C monomer includes a Z group which has the general formula



wherein R₂ is a hydrogen atom or a lower alkyl group, R₃ is a lower alkyl group, n is an integer from 20 to 500 and R₄ is a monovalent radical selected from the group consisting of

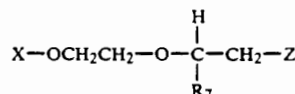
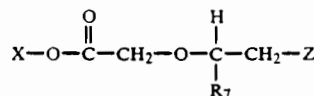
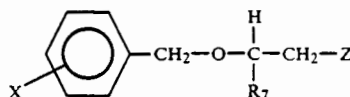
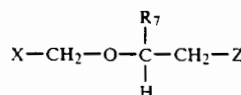


and $-CO_2R_6$ wherein R₅ is a hydrogen atom or a lower alkyl group and R₆ is a lower alkyl group. Preferably the C monomer has a general formula selected from the group consisting of



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wherein R₇ is a hydrogen atom or a lower alkyl group.

The vinyl terminated polymeric monomers are sometimes known as macromolecular monomers or macromonomers. Such monomers are known and may be prepared by the method disclosed in U.S. Pat. Nos. 3,786,116, and 3,842,059, Milkovich et al., the disclosures of which are incorporated herein by reference.

The binder copolymer must have a relatively high cohesive strength in order for the final particulate adhesive to exhibit the full reduction in adhesive transfer. One conventional way to increase cohesive strength is to increase the molecular weight. However, for an aerosol adhesive to exhibit satisfactory spray deposition, dispersions must be within a specific rheological window. For a fixed quantity of microspheres (or particles), the rheological behavior is primarily controlled by amount of binder copolymer present, and its molecular weight. Molecular weights which are too high become difficult to spray, i.e., they exhibit stringing and cobwebbing, resulting in very nonuniform coatings, whereas excessively low molecular weight results in misting and overspray.

Another method of achieving high cohesive strength in polymers is to utilize crosslinking with high molecular weight polymers, which can be detrimental to aerosol sprayability. Surprisingly, the use of preferred amounts of a high cohesive strength binder copolymer containing both a polar monomer, and a high T_g macromonomer satisfies the cohesive strength requirements. Phase separation of the macromonomer enhances cohesive strength even in lower molecular weight materials. It is believed that this cohesive strength helps to bind the microspheres more firmly, thereby reducing transfer.

Compositions of the invention therefore exhibit decreased adhesive transfer for increased peel adhesion while retaining excellent sprayability.

The cohesive strength can be ascertained by Dynamic Mechanical Analysis of the macromonomer-containing binder copolymers to determine the shear storage modulus (G'). See, e.g., S.L. Rosen, *Fundamental Principles of Polymer Materials*, pg 259, Wiley-Interscience, 1982. The shear storage modulus represents the stored elastic energy when a polymer sample is stressed at a given strain rate. The binder copolymer should have a shear storage modulus of at least about 1.0×10^5 Pascals, preferably about 1.10×10^5 Pascals, most pref-

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erably about 1.20×10^5 Pascals, when measured at 3 Hz and 22° C.

The binder copolymer is prepared by free radical polymerization as described, e.g., in U.S. Pat. No. 4,554,234 (Husman et al.), or D. Satas *Handbook of PSA Technology*, 2nd Ed., p. 908, Van-Norstrand-Rheinhold, NY, 1989, incorporated herein by reference.

The particulate pressure-sensitive adhesive of the invention is made by combining a dispersion of hollow microspheres with a solution of the binder copolymer. Typically, binder copolymer is used at a ratio of about 1% to about 30%, based on the dry weight of the hollow microspheres. Preferred ranges are dependent on the inherent viscosity ("I.V.") of the binder copolymer selected. For aerosol applications, the preferred amount of binder copolymer is from about 10% to about 25% for binder copolymers having I.V.'s in the range of from 0.4 to 0.8 dl/g, and for those having I.V.'s in the range of 0.8 to 1.2 dl/g, the preferred range is from about 3% to about 15%.

Suitable backing materials for the solvent based coatings include paper, plastic films, cellulose acetate, ethyl cellulose, woven or nonwoven fabric formed of synthetic or natural materials, metal, metallized polymeric film, ceramic sheet material, and the like. Surprisingly, the use of compositions of the invention eliminates the necessity of priming the backing, even paper, prior to coating of the microspheres. Previously, such priming was necessary to achieve an acceptable level of adhesive transfer.

Where an aerosol spray adhesive is desirable, an aerosol premix is made by combining a dispersion of hollow microspheres in isohexane or the like, with from about 1% to about 30% binder copolymer based on the dry weight of the hollow microspheres. The binder polymer is typically added in a solvent. This premix is then added to an aerosol container and the container charged with a suitable propellant to give a final solids content of about 3%–15%.

Dispersions of the particulate adhesive in the organic liquid as described above, may be sprayed by conventional techniques without cobwebbing or may be incorporated in aerosol containers with suitable propellants such as Dymel TM, alkanes, alkenes, or chlorofluorocarbons, e.g., Freons TM, compressed gases, and the like. The repositionable pressure-sensitive adhesive of the invention provides a degree of peel adhesion which permits separation, repositioning, and rebonding, as well as excellent adhesive transfer characteristics.

Useful premix formulae have a solids content of from about 5% to about 20%, preferably from about 10% to about 16%.

Properties of the pressure-sensitive adhesives of the invention may be altered by addition of tackifying resin and/or plasticizer. Preferred tackifiers for use herein include hydrogenated rosin esters commercially available from companies such as Hercules Inc., under such trade names as Foral TM, and Pentalyn TM. Individual tackifiers include Foral TM 65, Foral TM 85, and Foral TM 105. Other useful tackifiers include those based on t-butyl styrene. Useful plasticizers include dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate, and the like.

It is also within the scope of this invention to include various other components, such as pigments, fillers, stabilizers, or various polymeric additives.

The pressure-sensitive adhesives of the invention have been found to show little microsphere transfer,

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thereby reducing or even eliminating the transfer problems disclosed by the prior art. These pressure-sensitive adhesives also provide excellent sprayability and greater peel adhesion for a given coating weight than do prior art repositionable pressure-sensitive adhesives which are solid microsphere-based.

Test Methods

The following tests have been used to evaluate compositions of the invention. All percentages, parts and ratios are by weight unless specifically stated otherwise.

Adhesive Coating Weight

A 2.54 cm. by 5.08 cm. piece of preweighed (W1) acetate film is taped to the edge of a piece of paper. Adhesive is sprayed in a steady and uniform manner across the paper and acetate film. The film is then dried first at 52° C for one hour followed by drying at room temperature (about 22° C) for one hour and reweighed (W2). The difference between the starting weight (W1) and the final weight (W2) is determined to be the adhesive coating weight for both substrates expressed in grams per 12.9 square centimeters.

Peel Adhesion

Peel adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in grams per centimeter (cm.) width of coated sheet. The procedure followed is:

A strip 1.27 cm. in width of the coated sheet is applied to the horizontal surface of a clean glass test plate with at least 12.7 lineal cm. in firm contact. A 2 kg. hard rubber roller is used to apply the strip. The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 180 degrees. The free end is attached to the adhesion tester load cell. The glass test plate is clamped in the jaws of a tensile testing machine which is capable of moving the plate away from the load cell at a constant rate of 2.3 meters per minute. The load cell reading in grams is recorded as the tape is peeled from the glass surface. The data is reported as the average of the range of numbers observed during the test in grams per centimeter width of strip.

Adhesive Transfer

"Adhesive transfer force" is that force necessary to cause a failure of the transferred adhesive. Therefore, a high value for this force is undesirable, as it would indicate a higher amount of adhesive had been transferred (therefore having higher adhesion). The lower the value, the lower the amount of adhesive transfer. This test is very sensitive at amounts of transfer up to about 25%; a small increase in adhesive transfer results in a relatively large increase in the force required to cause failure. After this level, a plateau of separation force is reached such that additional amounts of transfer result in smaller increases in the necessary force to cause failure of the adhesive.

In this test, coated sheet material was adhered to a marked area of 60–80 lb. clay-coated paper, a commercially available paper for the printing industry, for a few seconds using a mechanical rolling action provided by an IMASS Slip Peel Tester and then removed by hand at a 90 degree angle. A 3.2 cm. wide strip of polyethylene terephthalate polyester film was then adhered to the clay-coated paper by mechanical means (above) to pro-

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vide a composite having a 20 cm. long overlap. The composite is removed from the Peel Tester and the claycoated paper end is clamped in the upper jaw of an Instron™ tensile tester and the polyester film end is clamped in the lower jaw. Using a crosshead separation speed of 2.5 cm. per minute, the peak separation force for the sample is determined and reported as grams.

Inherent Viscosity Measurement

Inherent viscosity is measured by conventional means using a Cannon-Fenske #50 viscometer in a water bath controlled at 25° C to measure the flow time of 10 milliliters of a polymer solution (0.2 g. of polymer per deciliter of ethyl acetate). The inherent viscosity (I.V.) is reported as deciliter per gram (dl/g).

The following examples are illustrative in nature, and are not intended to limit the invention in any way. The scope of the invention is that defined by the claims only.

Preparation of the Hollow Microspheres

The hollow microspheres used in the examples were prepared by one of the following methods.

In a resin reactor equipped with mechanical stirrer, condenser, and inlet-outlet for vacuum and inert gases, 450 parts of deionized water, 141 parts of isooctyl acrylate, 9.0 parts of acrylic acid and 0.5 part of benzoyl peroxide were charged. Vacuum was applied to evacuate the reactor atmosphere, and the reactor was then purged with an inert gas (e.g., argon or nitrogen). The agitation was set to 400 RPM and when the initiator had dissolved, 1.5 parts of ammonium lauryl sulfate ("Standapol A", Henkel AG) were added. The temperature of the reactor was raised to 60° C and maintained at such temperature for 22 hours. An inert gas purge was maintained during the polymerization. After the 22 hour period, the suspension was allowed to cool to room temperature. The reactor was then emptied and the suspension filtered. Optical microscopy revealed hollow microspheres from about 4 to about 90 micrometers in diameter suspended in water. The majority of the microspheres contained a central cavity of at least 30% of the diameter of the microsphere. The microspheres were isolated by addition of a 0.3% aqueous solution of barium chloride, filtered and dispersed in acetone-isohexane.

Hollow microspheres were also made as described above, except that the polymerization temperature was 65° C, and the polymerization period was 7.5 hours, and the agitation speed of the agitator was 95 RPM.

Preparation of the Macromonomer-Containing Binder Copolymer

In a glass reaction bottle, 8 grams of a 10,000 molecular weight methacrylate-terminated polystyrene macromonomer was combined with the monomers listed in Table A, 300 grams of ethyl acetate, 0.6 grams of the initiator, Vazo™ 64, and carbon tetrabromide dissolved in isooctyl acrylate. The percentages of carbon tetrabromide shown in Table A are based on the total amount of monomers (200g of monomers mixture). The bottle was then purged with nitrogen, sealed and tumbled in a water bath at 55° C for 24 hours.

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TABLE A

| Macromonomer Containing Binder Copolymer | IOA g | ACM g | NVP g | AA g | NOACM g | CBr ₄ % | I.V. |
|---|----------|----------|----------|---------|------------|-----------------------|------|
| A | 184 | 8.0 | — | — | — | 0.020 | 1.02 |
| B | 184 | 8.0 | — | — | — | 0.050 | 0.76 |
| C | 184 | 8.0 | — | — | — | 0.090 | 0.61 |
| D | 184 | 8.0 | — | — | — | 0.125 | 0.50 |
| E | 184 | 8.0 | — | — | — | 0.175 | 0.40 |
| F | 184 | — | — | 8.0 | — | 0.075 | 0.57 |
| G | 162 | — | 30.0 | — | — | 0.075 | 0.58 |
| H | 172 | — | — | — | 20.0 | 0.075 | 0.55 |

IOA: isooctyl acrylate

ACM: acrylamide

NVP: N-vinyl pyrrolidone

AA: acrylic acid

NOACM: n-octyl acrylamide

Dynamic Mechanical Thermal Analysis (DMTA)

Polymer specimens were prepared by solvent casting relatively thick films, ca. 2 mm in thickness, that were carefully air dried at room temperature for seven days, followed by 24 hour drying in vacuo. The shear storage modulus was then determined using a Polymer Laboratories DMTA Mark I, (Amherst Fields Research Park, Amherst, MA 01002) at 3 Hz and 22°. The data for a series of polymers is given in Table B below.

TABLE B

| Compositions | I.V. | G' (Pa × 10 ⁵) | T(°C) |
|---|------|----------------------------|-------|
| IOA/ACM/MAC ^{1,3} (92/4/4) | 0.61 | 1.205 | 23 |
| IOA/ACM/MAC ² (92/4/4) | 1.02 | 1.253 | 22 |
| IOA/AA/MAC ¹ (92/4/4) | 0.60 | 1.050 | 22 |
| IOA/NVP/MAC ¹ (81/15/4) | 0.58 | 0.978 | 23 |
| IOA/NOACM/MAC ¹ (81/10/4) | 0.55 | 0.529 | 22 |

¹Polystyrene macromonomer, MW = 10,000²Polysar macromonomer, C-4500³IOA, iso-octyl acrylate; ACM, acrylamide, AA, acrylic acid; NVP, N-vinyl pyrrolidone; NOACM, N-octylacrylamide

EXAMPLES

Comparative Examples 1C-4C

The comparative compositions were prepared by first dispersing the hollow microspheres in a solvent mixture of 60:40 by weight isohexane:acetone to yield a 12% dispersion of microspheres in the solvent to obtain an aerosol premix. This premix was then added to a 6 fluid ounce metal aerosol container fitted with the appropriate gaskets, valves, and a spray-button actuator, and the aerosol container was then charged with an isobutane propellant (A-31, isobutane having 31 psig at 70° F) to bring the total solids to 5-6%. Table 1 shows the peel adhesion and adhesive transfer force, along with the coating weights. The substrate used was standard white copier paper.

TABLE 1

| Example No. | Percent Copolymer | Adhesive Coating g/12.9 cm ² | Peel Adhesion g/cm | Adhesive Transfer Force g |
|-------------|-------------------|---|--------------------|---------------------------|
| 1C | 0 | 0.002 | 9.13 | 7,200 |
| 2C | 0 | 0.003 | 17.01 | 7,371 |
| 3C | 0 | 0.004 | 31.18 | 8,023 |

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TABLE 1-continued

| Example No. | Percent Copolymer | Adhesive Coating g/12.9 cm ² | Peel Adhesion g/cm | Adhesive Transfer Force g |
|-------------|-------------------|---|--------------------|---------------------------|
| 4C | 0 | 0.005 | 32.44 | 8,108 |

Examples 1-12

These examples illustrate the effect of the composition of the macromonomer-containing binder copolymer on adhesive transfer.

The compositions were prepared by first dispersing the hollow microspheres in a solvent mixture of 60:40 by weight isohexane:acetone to yield a 12% dispersion of microspheres in the solvent. An ethyl acetate solution of the macromonomer-containing binder copolymer with the composition and I.V. described in Table A was prepared and added to the microsphere dispersion to obtain an aerosol premix. This premix was then added to a six-fluid ounce metal aerosol container fitted with the appropriate gaskets, valves, and a spray-button actuator, and the aerosol container was then charged with an isobutane propellant (A-31, isobutane having 31 psig at 70° F.) to bring the total solids to 5-6%. The amounts of macromonomer-containing binder copolymer based on dry weight of hollow microspheres, the peel adhesion and the adhesive transfer force are shown in Table 2. The substrate used was standard white copier paper. The coating weight for the samples is about 0.005g/12.9cm².

TABLE 2

| Example No. | I.V. | % by Wt Copolymer | Peel Adhesion g./cm. | Adhesive Transfer Force (g.) |
|---|------|-------------------|----------------------|------------------------------|
| Macromonomer-Containing Binder Copolymer C | | | | |
| 1 | 0.61 | 15 | 37.48 | 3,643 |
| 2 | 0.61 | 20 | 36.54 | 1,956 |
| 3 | 0.61 | 25 | 40.16 | 1,389 |
| Macromonomer-Containing Binder Copolymer F | | | | |
| 4 | 0.57 | 15 | 22.20 | 3,912 |
| 5 | 0.57 | 20 | 25.35 | 3,061 |
| 6 | 0.57 | 25 | 28.03 | 3,940 |
| Macromonomer-Containing Binder Copolymer G | | | | |
| 7 | 0.58 | 15 | 22.05 | 4,493 |
| 8 | 0.58 | 20 | 27.72 | 5,301 |
| 9 | 0.58 | 25 | 29.13 | 4,777 |
| Macromonomer-Containing Binder Copolymer H | | | | |
| 10 | 0.55 | 15 | 24.25 | 3,289 |
| 11 | 0.55 | 20 | 24.36 | 4,772 |
| 12 | 0.55 | 25 | 29.40 | 3,875 |

As can be seen from the above table, compositions of the invention, i.e., those including a macromonomer-containing binder copolymer show dramatically reduced force required to cause the transferred adhesive to fail. This indicates that the amount of transferred adhesive for compositions of the invention is reduced by an equally sizable percentage.

Examples 13-17

The compositions were prepared as described in Examples 1-12, except that various types of macromonomer-containing binder copolymer were used. Table 3 shows the adhesive transfer force as a function of the I.V. of the macromonomer-containing binder copolymer, and amount of macromonomer-containing binder copolymer. Again, the substrate was standard white copier paper.

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TABLE 3

| | | Adhesive Transfer Force (g.) | | | | |
|-------------|-------------|--|-------|-------|-------|-------|
| | | % Macromonomer-Containing Binder Copolymer | | | | |
| Example No. | Type (I.V.) | 5% | 10% | 15% | 20% | 25% |
| 13 | A (1.02) | 3,955 | 1,942 | 1,516 | — | — |
| 14 | B (0.76) | — | 2,963 | 2,112 | 1,871 | — |
| 15 | C (0.61) | — | — | 3,643 | 1,956 | 1,389 |
| 16 | D (0.50) | — | — | 3,579 | 2,679 | 3,416 |
| 17 | E (0.40) | — | — | 2,750 | 4,479 | 2,126 |

Examples 18-22

The compositions were prepared as described in Examples 1-12, except that Macromonomer-Containing Binder Copolymer C, having an I.V. of 0.61 was used. Table 4 shows the adhesive transfer force for a variety of coating weights. The substrate used was standard white copier paper.

TABLE 4

| Example No. | Percent Binder Copolymer | Adhesive Coating g/12.9 cm ² | Peel Adhesion g/cm | Adhesive Transfer Force (g.) |
|-------------|--------------------------|---|--------------------|------------------------------|
| 18 | 20 | 0.0030 | 19.69 | 1,049 |
| 19 | 20 | 0.0037 | 30.71 | 1,276 |
| 20 | 20 | 0.0055 | 39.69 | 468 |
| 21 | 20 | 0.0063 | 50.08 | 680 |
| 22 | 20 | 0.0098 | 66.93 | 71 |

Examples 23-35

In these examples, peel adhesion and adhesive transfer force were measured from a variety of conventional substrates, including assorted types of papers and films. The substrate was sprayed with an aerosol composition similar to that described in Examples 18-22. The results are shown in Table 5.

TABLE 5

| Example No. | Substrate | Peel Adhesion g/cm | Adhesive Transfer Force g. |
|-------------|---------------------|--------------------|----------------------------|
| 23 | Magazine | 64.02 | 3,856 |
| 24 | Photo Layout | 58.11 | 2,367 |
| 25 | Vellum | 38.66 | 1,262 |
| 26 | Foil | 53.86 | 872 |
| 27 | Parchment | 22.99 | 1,233 |
| 28 | Construction | 20.71 | 872 |
| 29 | Tracing paper | 34.02 | 1,914 |
| 30 | Art Kraft | 26.14 | 496 |
| 31 | Lindsey layout bond | 6.54 | 291 |
| 32 | Crepe Paper | 2.52 | 269 |
| 33 | Wrapping Paper | 25.04 | 191 |
| 34 | Litho Mask | 70.87 | 142 |
| 35 | Exposed Litho Film | 70.87 | 2,055 |

What is claimed is:

1. A repositionable pressure-sensitive adhesive comprising from about 70% to about 99% of:

(a) hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres comprising at least one alkyl acrylate or alkyl methacrylate ester, a majority of the microspheres having one or more interior voids having a diameter of at least about 10% of the diameter of the microsphere; and

(b) correspondingly, from about 30% to about 1% of a binder copolymer comprising an elastomeric polymeric backbone having pendant therefrom polymeric moieties, said backbone containing re-

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peating A and C monomers and from about 1% to about 20% B monomers, wherein

A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms, with the average number of carbon atoms being about 4-12, said A monomer comprising from about 50% to about 98% of said monomers;

B is a polar monomer copolymerizable with said monomeric acrylic acid ester;

C is a monomer having the general formula $X-(Y)_n-Z$, wherein X is a vinyl group copolymerizable with said A and B monomers,

Y is a divalent linking group, where n is zero or 1, and

Z is a monovalent polymeric moiety having a T_g greater than 20° C, and a molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions, C comprising

from about 1% to about 30% of said monomers, wherein said binder copolymer has a shear storage modulus of at least about 1×10^5 Pascals at 3 Hz, and 22° C.

2. A repositionable pressure-sensitive adhesive according to claim 1 wherein said microspheres further comprise at least one polar monomer.

3. A repositionable pressure-sensitive adhesive comprising from about 70% to about 99% of:

(a) hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres comprising

(i) at least about 85 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester; and

(ii) up to about 15 parts by weight of at least one polar monomer, a majority of the microspheres having one or more interior voids having a diameter of at least about 30% of the diameter of the microsphere, and

(b) correspondingly, from about 30% to about 1% of a binder copolymer comprising an elastomeric polymeric backbone having pendant therefrom polymeric moieties, said backbone containing repeating A and C monomers and from about 1% to about 20% B monomers, wherein

A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms, with the average number of carbon atoms being about 4-12, said A monomer comprising from about 50% to about 98% of said monomers;

B is a polar monomer copolymerizable with said monomeric acrylic acid ester;

C is a monomer having the general formula $X-(Y)_n-Z$, wherein X is a vinyl group copolymerizable with said A and B monomers,

Y is a divalent linking group, where n is zero or 1, and

Z is a monovalent polymeric moiety having a T_g greater than 20° C, and a molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions, C comprising from about 1% to about 30% of said monomers,

wherein said binder copolymer has a shear storage modulus of at least about 1×10^5 Pascals at 3 Hz and 22° C.

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4. A repositionable pressure-sensitive adhesive according to claim 1 wherein said binder copolymer has a shear storage modulus of at least about 1.1×10^5 Pascals at 3 Hz and 22° C.

5. A repositionable pressure-sensitive adhesive according to claim 1 wherein said monomer B in said binder copolymer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, N-vinyl pyrrolidone, acrylamide, methacrylamide, acrylonitrile and methacrylonitrile.

6. A repositionable pressure-sensitive adhesive according to claim 1 wherein said binder copolymer has an inherent viscosity in the range of from 0.4 to 0.8 dl/g, and comprises from about 10% to about 25% of said adhesive.

7. A repositionable pressure-sensitive adhesive according to claim 1 wherein said binder copolymer has an inherent viscosity in the range of from 0.8 to 1.2 dl/g, and comprises from about 3% to about 15% of said adhesive.

8. A repositionable spray pressure-sensitive adhesive comprising a composition according to claim 1 and further comprising a propellant selected from the group consisting of alkanes, alkenes, chlorofluorocarbons, and compressed gases.

9. A repositionable spray pressure-sensitive adhesive according to claim 8 having a solids content of from about 3% to about 15%.

10. A repositionable spray pressure-sensitive adhesive according to claim 9 having a solids content of from about 4 to about 8%.

11. An organic dispersion comprising an organic carrier liquid and

(a) hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric microspheres comprising at least one alkyl acrylate or alkyl methacrylate ester, a majority of the microspheres having one or more interior voids having a diameter of at least about 10% of the diameter of the microsphere; and

(b) a binder copolymer comprising an elastomeric polymeric backbone having pendant therefrom polymeric moieties, said backbone containing repeating A and C monomers and from about 1% to about 20% B monomers, wherein

A is a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 1 to 14 carbon atoms, with the average number of carbon atoms being about 4-12, said A monomer comprising from about 50% to about 98% of said monomers;

B is a polar monomer copolymerizable with said monomeric acrylic acid ester;

C is a monomer having the general formula $X-(Y)_n-Z$, wherein X is a vinyl group copolymerizable with said A and B monomers,

Y is a divalent linking group, where n is zero or 1, and

Z is a monovalent polymeric moiety having a T_g greater than 20° C, and a molecular weight in the range of about 2,000 to about 30,000, and being essentially unreactive under copolymerization conditions, C comprising from about 1% to about 30% of said monomers,

wherein said binder copolymer has a shear storage modulus of at least about 1×10^5 Pascals at 3 Hz and 22° C.

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12. A sheet material having coated on at least a portion thereof the organic dispersion of claim 11.

13. A sheet material coated with the repositionable pressure-sensitive adhesive of claim 1.

14. A repositionable pressure-sensitive adhesive comprising the organic dispersion of claim 11.

15. A repositionable pressure-sensitive adhesive according to claim 1 wherein said hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric adhesive microspheres comprise:

(a) at least about 85 parts by weight of at least one alkyl acrylate ester selected from the group consist-

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ing of isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate and n-butyl acrylate, and

(b) correspondingly, up to about 15 parts by weight of at least one polar monomer selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, and salts thereof.

16. A repositionable pressure-sensitive adhesive according to claim 15 wherein said alkyl acrylate is isooctyl acrylate, and said polar monomer is acrylic acid.

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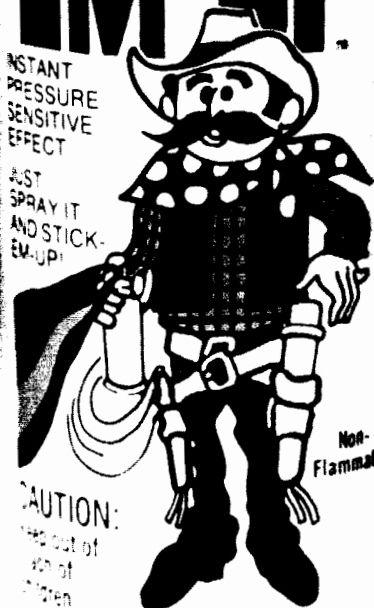
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Simple to use

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Cardboard, Foil, Wood,
Plastic Sheeting, etc.

HOBBY & CRAFT:

Adhere Glitter and Sand,
Decoupage and Collage

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Adhere Leather, Fabric,
Wallpaper, Shelfpaper,
Labels, Felt Padding,
Carpet Squares,
Mount Posters,
Pictures, Memos, etc.

DIRECTIONS

Shake well before using. Expose under part of surface you wish to make pressure sensitive. Holding can 12" away, spray surface. Do not overspray and allow a few seconds to dry. Your surface is now pressure sensitive. Press lightly on top of surface and it will stick. Item can be lifted and repositioned with ease.

AFTER USING—Turn can upside down and press tip until spray is clear of adhesive.

PERMANENT BOND—When using as a permanent bond, spray area and apply before allowing to dry.

NON-PERMANENT—Spray area, allow to dry before applying.

CAUTION:

Use with adequate ventilation. Avoid prolonged inhalation of vapor. Contents of can under pressure. Do not dispose of can in incinerator. Store below 120° F.

NOTICE TO PURCHASER: Manufacturer's only obligation shall be to replace such quantity of the product proved to be defective. User shall determine the suitability of the product for his intended use and assume all risk and liability in connection therewith.

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DIRECTIONS

Expose under part of surface you wish to make pressure sensitive. Holding can 12" away, spray surface. Do not overspray and allow a few seconds to dry. Your surface is now pressure sensitive. Press lightly on top of surface and it will stick. Item can be lifted and repositioned with ease.

CAUTION:

Use with adequate ventilation. Avoid prolonged inhalation of vapor. Contents of can under pressure. Do not dispose of can in incinerator. Store below 120° F.

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- PHOTO ALBUMS, SIGN MOUNTING, FRAMING
- SCHOOL PROJECTS
- WALL-PAPERING, SHELF PAPERING, VINYL TILING, UPHOLSTRY REPAIR, CARPET TILING
- FABRICS, WOOD, GLASS, METAL, PLASTIC, CARDBOARD, RUBBER, PAPER

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any surface
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AND STICK-
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| SHIP VIA | F.O.B. | TERMS | DELIVERY REQUIRED | JOB OR REQ. NO. |
|-----------|--|--------|-------------------|-----------------|
| - pick-up | - | 370 10 | ASAP | - |
| QUANTITY | DESCRIPTION | PRICE | UNIT | AMOUNT |
| 100cs | 802 stick - em up (cost 93¢) | | | 1116.00 |
| 25cs | 1602 stick - em up (cost 131¢) | | | 393.00 |
| 2cs | 802 stick - em up for samples | N/C | N/C | |
| | | total | | 1509.00 |
| | Initial Private Company name on labels | | | 250.00 |
| | No charge for when order ready | CARDS | | 75.00 |
| | Future Private call Esther | | | |
| | Labbing to arrange pick up | total | | 1834.00 |
| | For same company | | | |
| | Just charged for plate changes | | | |

IMPORTANT

ABOVE ORDER NUMBER MUST APPEAR ON ALL CORRESPONDENCE, INVOICES, PACKAGES AND SHIPPING PAPERS. NOTIFY US IMMEDIATELY IF YOU ARE UNABLE TO SHIP COMPLETE ORDER BY DATE SPECIFIED. YOUR ACCEPTANCE OF THIS ORDER IS YOUR WARRANTY TO US THAT YOU ARE COMPLYING WITH THE U. S. FAIR LABOR STANDARDS ACT OF 1938, AS AMENDED, AND WE RESERVE THE RIGHT TO REFUSE MERCHANDISE NOT IN STRICT ACCORDANCE WITH THIS ORDER.

By

Bernie Scha

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5162**Sold To Alco Photo Supply Corporation131-27 Fowler AveFlushing, New York 11355Shipped To Picked up Esther

DATE

5/14/75

CUSTOMER'S ORDER

A. Amron

SALESMAN

3% Net 10 Days

TERMS

N.Y.

F.O.B.

N.Y.

SHIPPED VIA

Pick up

| | | | |
|---|--|------|--|
| 100 Cs. | 7oz Stickem-up spray adhesive 12 cans per case Private labeled | . 93 | 1116.00 |
| 25 Cs. | 14oz Stickem-up spray adhesive 12 cans per case private labeled | 1.31 | 393.00 |
| 150 | header cards private labeled (Hold charge) | | |
| * * | All private labling charges held. (Speak to salesman) | | |
| Total Amount Due | | | \$1509.00 |
| <i>Paul</i> <i>5-30-75</i> <i>OK #510</i> <i>Rec'd 1463²³</i> | | | <i>45²⁷ Ast</i> <i>→</i> |
| THANK YOU..... | | | |

Rediform 75 725

Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.

31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5171**

Sold To Applebaums Food Market Inc.

222 Plato Blvd.

St. Paul Minnesota 55107

Shipped To Merrill Sundholm

DATE
5/14/75

CUSTOMER'S ORDER

77

SALESMAN

A Amron

COD TERMS

NET 2 days

NY F.O.B.

SHIPPED VIA

UPS

1 Cs. ~~Sticker-up~~ Spray Adhesive

14.94

14.94

Shipping & Handling

1.50

Total Amount Due

\$16.44

THANK YOU.....

Rediform® 75 725
Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5175**

Sold
To

Paul D. Golub

7 Winchester Place

Loudonville New York 12211

Shipped To

SAME

DATE

5/14/75

CUSTOMER'S ORDER

73

SALESMAN

A AMron

TERMS

Pre Paid

N.Y.B.

SHIPPED VIA

UPS

| | | | | |
|-------|--------------------------------|-------|--|---------|
| 1 Cs. | 14oz Sticken-up spray adhesive | 23.88 | | |
| | | | | prepaid |
| | Shipping & handling | | | 1.50 |
| | Total Amount Due | | | \$1.50 |
| | THANK YOU..... | | | |
| | | | | |
| | | | | |
| | | | | |

Rediform® 75 725

Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5174**

Sold To **Bells Market**

Mainon Inc.
5305 Main Street
Williamsville New York 14221

Jack Mesches

Shipped To

DATE

5/14/75

CUSTOMER'S ORDER

74

SALESMAN

AAMRON

TERMS

"Net Cod 2 Days"

NY

F.O.B.

SHIPPED VIA

UPS

1 Cs. Stickem-up Spray Adhesive

14.94

14.94

Shipping & Handling

1.50

Total Amount Due

\$16.44

THANK YOU.....

172852

6/1/75

Rediform® 75 725

Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5170**

Sold To **Service Food Stores Inc.**

4131 West Capital Drive

Milwaukee Wisc. 53216

Shipped To **Dallas Show Ordered**

5/14/75 DATE

77 CUSTOMER'S ORDER

A AMRON SALESMAN

Cod TERMS **NET 2 days**
NY F.O.B.

UPS SHIPPED VIA

| | | | | |
|--|-------------------------------|-------|---------|--|
| 1 Cs. | 7oz Sticker-up Spray adhesive | 14.94 | | |
| | | | 14.94 | |
| | Shipping & Handling | | 1.50 | |
| | Total Amount Due | | \$16.44 | |
| <p><i>paid in full</i></p> <p>THANK YOU.....</p> <p><i>6/2/75 ck #2039</i></p> | | | | |

Rediform* 75 725
 Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5169**

Sold To **A. Barney Moldovan A&M Foodland**

4th Street

Irwin Pa. 15642

Shipped To **Barney**

DATE
5/14/75

CUSTOMER'S ORDER
A. AMRON 78

SALESMAN
A AMRON

TERMS
Net 10 Days

F.O.B.
NY

SHIPPED VIA
UPS

1 Cs. 7oz Stickem-up spray adhesive

14.94

14.94

Shipping & Handling

1.50

Total Amount Due

\$16.44

THANK YOU

Rediform 75 725
 Poly Pak (50 sets) 7P 725

INVOICE

Handwritten: Paid full 5/15/75 CK #3958

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5168**

Sold To **Zehrs Markets Ltd.**
120 Ottawa Street North
Kitchener Ontario

Shipped To **Ron West**

DATE
5/14/75CUSTOMER'S ORDER
79SALESMAN
A. AmronTERMS
Cod **NET 2 days**F.O.B.
ny USA NYSHIPPED VIA
UBMAIL1 Cs. **7oz Stickem-up Spray adhesive****14.94****14.94****Shipping & Handeling****1.50****Total Due****\$16.44**

THANK YOU

Rediform' 7S 725
 Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.

31 SOUTH GROVE STREET

FREEPORT, NEW YORK 11520

No. **5167**

Sold To **Handy Andy Shop n Save Supermarket**

To

155 North 10th street

Indiana , Pa. 15701

Shipped To **Stanley Heinricher**

DATE

5/14/75

CUSTOMER'S ORDER

80

A. Amson SALESMAN

cod

TERMS

ny

F.O.B.

SHIPPED VIA
Ups

3 Cases 7oz Stickem-up spray adhesive

14.94

44.88

Shipping & Handling

2.50

Total Amount Due

\$47.30

THANK YOU

Rediform® 75 725
Poly Pak (50 sets) 7P 725

INVOICE

Handwritten:
Paid in full
5/27/75

No. 5166

Sold **Durso supermarkets**
To _____

2465 Broadway

New York, N.Y. 10025

Shipped To Connie Durso

5/14/75 DATE

CUSTOMER'S ORDER

SALESMAN
A. Axon

Net ^{TERMS} 10 Days

N.Y. F.O.B.

 SHIPPED VIA

Rediform® 7S 725
Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.

31 SOUTH GROVE STREET

FREEPORT, NEW YORK 11520

No. **5165**

Sold To

Price Chopper Supermarkets

501 Duaneburg Road

Schenectady, New York 12301

Shipped To

Neil Golub

DATE

5/14/75

CUSTOMER'S ORDER

82

SALESMAN
A. Anron

TERMS

Net 10 Days

F.O.B.

NY

SHIPPED VIA

ups

4 Cs.

7oz Sticken-up Spray adhesive

14.94

59.76

Shipping & Handeling

2.70

Total Amount due

\$62.46

Buyer Dave Younts

518 355 5000

THANK YOU

Rediform 75 725

Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5163**

Sold To **Steu Leonards Dairy**
30 Westport Ave
Norwalk, Conn. 06851

Shipped To **SAME**

DATE
~~7/15~~ **5/14/75**

CUSTOMER'S ORDER
BY PHONE

SALESMAN
A. Amron

TERMS
COD Net 2 Days
 F.O.B.

N.Y.

SHIPPED VIA

UPS

| | | | | |
|--------------|---|--------------|--|----------------|
| 2 Cs. | 7oz Stiken-up 12 cans per case | 14.94 | | |
| | (MINIMUM ORDER @ 2 cases for wholesale price) | | | 29.88 |
| | Shipping & Handling | | | 2.00 |
| | Total Amount Due | | | \$31.88 |
| | THANK YOU | | | |

Rediform® 75 725
 Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.

31 SOUTH GROVE STREET

FREEPORT, NEW YORK 11520

No. **5160**

Sold To

Boca Industries INC
31 South Grove St.
Freeport N.Y. 11520

Shipped To

SAME

DATE
5/14/75

CUSTOMER'S ORDER

A. AMERON

SALESMAN

C.O.D.

TERMS

F.O.B.

ME

SHIPPED VIA

2 Cases Stickem up 1402.

24 CANS

1.10

total Amount due

26.40

PAID

DELIVERED 5/14/75

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5155**

Sold To **Best Buy Variety Stores**
77 Quaker Ridge Road
New Rochelle N.Y 10804
 Shipped To **Richy**

914
235
1875

SENT
COPY
OUR DUPLICATE
5/14/75

DATE **3/17/75**
 CUSTOMER'S ORDER
 SALESMAN **RK**
 TERMS **N/T 10**
 F.O.B. **RK**
 SHIPPED VIA

Called
6/11/75
90 days
over

| | | | |
|----------------------------------|-----------------------|------|---------|
| 12 | Cans Stickem up 8 oz. | 1.25 | \$15.00 |
| Delivered By ARKAY SALES 3/17/75 | | | |
| Amount Due..... | | | \$15.00 |
| THANK YOU..... | | | |

OK #1869
 PAD
 6/16/75

Rediform* 75 725
 Poly Pak (50 sets) 7P 725

INVOICE

No. **5154**Sold
To**Gemini International, Inc.****1270 Broadway****New York, New York 10001**Shipped To **Same**

DATE

3/14/75

CUSTOMER'S ORDER

AA

SALESMAN

Net 10

TERMS

F.O.B.

SHIPPED VIA

6 Cases 8oz. Stick'Em Up**2 Cases 16oz. Stick'Em Up****\$ 11 22 \$ 67 32****4 17 88 \$ 35 76****Total Amount****\$103 08****On MEMO**Rediform® 75 725
Poly Pak (50 sets) 7P 725**INVOICE**212
947 5405
Barry
PruettGot Back 16oz
6/20/75 1 Day 8oz

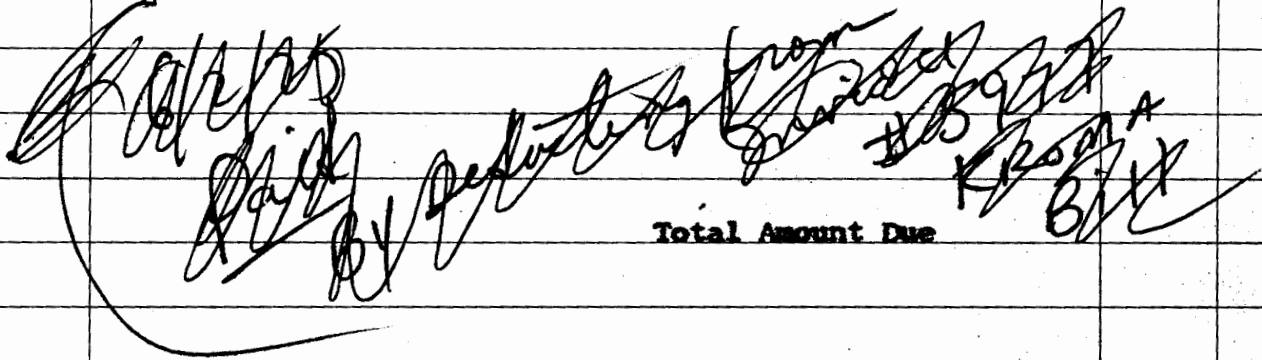
*Over Due Notice
7/2/75*

No. **5153**

Sold To **Kroma**
30 West 21st Street
New York, New York 10010

Shipped To _____

DATE
3/14/75
CUSTOMER'S ORDER
AA
SALESMAN
TERMS
F.O.B.
SHIPPED VIA

| | | | | | |
|---|--------------------|--------------|-----------|--------------|-----------|
| 4 Cases | Stick'Em Up | \$ 12 | 60 | \$ 50 | 40 |
|  | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| Total Amount Due | | | | \$ 50 | 40 |
| | | | | | |
| | | | | | |
| | | | | | |

Rediform® 7S 725
Poly Pak (50 sets) 7P 725

INVOICE

Cam-re Fair

1763 Grand Avenue

Baldwin, New York 11520

Shipped To Same

3/14/75

CUSTOMER'S ORDER

AA

SALESMAN

TERMS

F.O.B.

SHIPPED VIA

| | |
|--------|-------------|
| 1 Case | Stick'em Up |
|--------|-------------|

\$ 1.25

| |
|----------|
| \$ 15.00 |
|----------|

PAID BY CHECK

Rediform® 7S 725
Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5177**

Sold
To

Interphoto Corp.

23-20 Jackson Ave

Long Island City, New York 11101

Shipped To

Jerry Littman

*over the
notice 7/2/75
all
over
#30
212
392 7600*

DATE

5/19/75

CUSTOMER'S ORDER

Jerry Littman

SALESMAN

Alan Amron

TERMS

Net 10 Days

F.O.B.

Hand Carried

SHIPPED VIA

Hand Carried

| | | | |
|--|---|-------|---------|
| 4 Cs. | Stickem-up spray adhesive 7 oz. 12 per case | 14.94 | \$59.76 |
| | Shipping & handling | | n/c |
| <p><i>Paid in full</i></p> <p>THANK YOU</p> <p><i>8/5/75</i></p> <p><i>#19310</i></p> | | | |
| | | | |
| | | | |
| | | | |

Rediform 75 725

Poly Pak (50 sets) 7P 725

INVOICE

BARRY ALAN PRODUCTS, INC.
31 SOUTH GROVE STREET
FREEPORT, NEW YORK 11520

No. **5179**

Sold To John Revle Blok & Diaz Trading Co.
Post Office Box 659
Curacao NA.
SAME
 Shipped To _____

DATE
5/19/75
 CUSTOMER'S ORDER
John Revle
 SALESMAN
Alan Amron
 TERMS
Prepaid For Product
 F.O.B.
New York
 SHIPPED VIA
US MAIL

| | | | |
|-------|---------------------------------------|-------|-------|
| 1 Cs. | 7oz Sticken-up spray adhesive 12 cans | 14.94 | 14.94 |
| | deling | | 12.47 |
| | | | 27.41 |
| | at show for product | 14.94 | |
| | Amount due | 12.47 | |
| | | | |
| | | | |

12.47

